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SOLUBILITY. I.

BY R. C. BINGHAM.

The present paper presents the results of some experimental work performed in the Cavendish Laboratory, the work being preliminary to a more extended study of solubility.

All gases are completely miscible; liquids, therefore, afford an interesting field for study inasmuch as the liquid and gaseous states have been found to be continuous, but, of the enormous amount of work already done on solubility, the greater part has been confined to the study of a solid in a liquid, especially water. There are sufficient reasons, moreover, for believing that the solution of a solid may be more complex than the solution of a liquid, and that water may not show the phenomena of solution as simply as do some other liquids.

Alexejeff[1] was the first to make a systematic study of the solubility of liquids in liquids. He studied carefully the effect of variation of temperature upon the solubility of a few

[1] Wied. Ann., 28, 305 (1886).

pairs of immiscible liquids. He found that, in general, the solubility increased with the temperature until, in a few cases, the solubility became infinite, *i. e.*, the liquids became completely miscible. This temperature was called by Masson[1] "the critical solution temperature," in analogy to the ordinary critical solution temperature. Later, Guthrie[2] found that in certain instances the solubility increased with falling temperature until there was complete miscibility. Such a temperature has been called, therefore, a "lower critical solution temperature."

Since Alexejeff's work, several others[3] have studied carefully certain pairs of liquids, but it does not seem to have occurred to any one as being worth while to make a systematic examination of a considerable number of representative liquids, to learn, if possible, under what conditions an immiscible combination may be looked for, and also when a change of temperature will cause the immiscible pairs to become miscible.

To test the above point and to accumulate data for further work, it seemed advisable to the author to make all the possible combinations with a certain number of pure liquids.

METHOD OF WORK.

Thick-walled glass tubing of about 2 mm. internal diameter was carefully cleaned by the use of chromic acid mixture, washed and dried. Several hundred small tubes, 6–7 mm. long, were then made, care being taken not to introduce moisture during the sealing off. The tubes were kept over phosphorus pentoxide until ready for use.

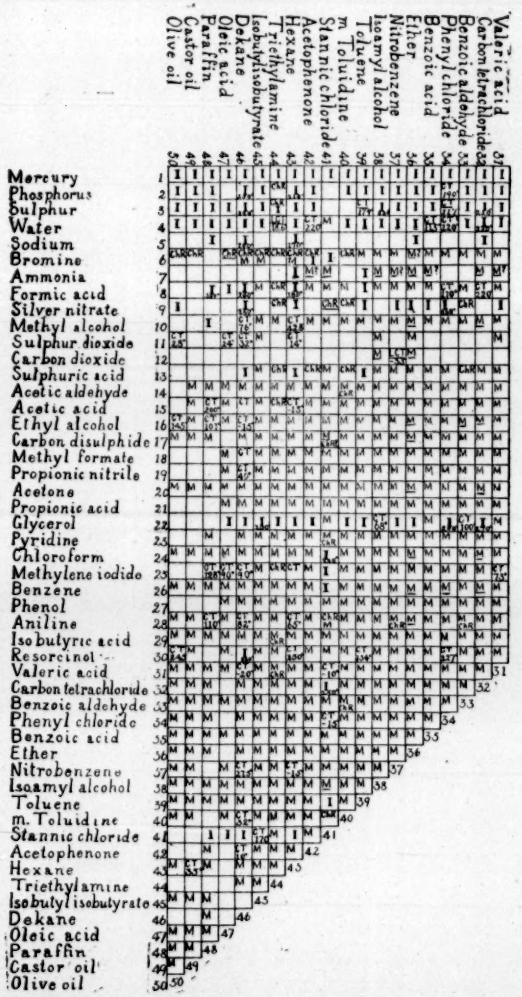
The substances employed were, as far as practicable, the best that Kahlbaum provides. In order to work readily with small quantities, I constructed a burette of small bore, graduating and calibrating it carefully. The tip was drawn out to a long, narrow tube, suitable for introducing the liquids to the bottom of the small tubes as well as for filling the burette without

[1] Nature, Feb. 12, 1891; Z. physik. Chem., 7, 500 (1891).
[2] Phil. Mag. [5], 18, 29, 499 (1884).
[3] Rothmund: Z. physik. Chem., 26, 433 (1898). Hudson: *Ibid.*, 47, 113 (1904).

having the preparations come into contact with the air. The top of the burette was continually connected with a calcium chloride drying-tube, by means of a rubber tube of considerable length. The tubes were stoppered immediately after adding 1 of the components and the result of putting the 2 components together was noted as soon as possible, even during the process of bringing them together. Equal volumes of the 2 components were added together throughout. It was necessary to work with phenol in a pipette on account of its tendency to solidify. Resorcinol, benzoic acid, silver nitrate, sodium, phosphorus and sulphur were all added in the solid state. When necessary, the tubes were sealed before the blowpipe and then heated in a water or paraffin bath until mixture ensued, if possible. In some cases chemical reaction began at high temperatures, and in one case resulted in a severe explosion. The tubes were also cooled in an ice and salt mixture. Some 200 were cooled in liquid air.

In the table the results of the experiments are given in concise form. The substances are arranged in the order of their molecular volumes. Those pairs which mixed completely are marked M, those which were immiscible at all the temperatures which were employed are marked I, in some cases with the temperature to which they were heated added. Upper critical solution temperatures are marked CT and lower critical solution temperatures with LCT, with the, roughly approximate, temperature at which the substances become miscible. ChR denotes that a chemical reaction took place between the components when brought together. In case this combination was very slow, conclusions in regard to miscibility could be obtained which are of interest. These cases are marked $\frac{M}{ChR}$; or $\frac{ChR}{M}$ in case the combination took place so rapidly that the results were in doubt. The results in italics were taken mainly from the papers of Rothmund,[1] Zawidski,[2] and the author,[3] also Watts' "Dictionary" and

[1] Z. physik. Chem., **26**, 433 (1898).
[2] *Ibid.*, **35**, 202.
[3] THIS JOURNAL, **34**, 481 (1905); **35**, 195 (1906).


Mercury
Phosphorus
Sulphur
Water
Sodium
Bromine
Ammonia
Formic acid
Silver nitrate
Methyl alcohol
Sulphur dioxide
Carbon dioxide
Sulphuric acid
Acetic aldehyde
Acetic acid
Ethyl alcohol
Carbon disulphide
Methyl formate
Propionic nitrile
Acetone
Propionic acid
Glycerol
Pyridine
Chloroform
Methylene iodide
Benzene
Phenol
Aniline
Isobutyric acid
Resorcinol
Valeric acid
Carbon tetrachloride
Benzoic aldehyde
Phenyl chloride
Benzoic acid
Ether
Nitrobenzene
Isoamyl alcohol
Toluene
m. Toluidine
Stannic chloride
Acetophenone
Hexane
Triethylamine
Isobutyl isobutyrate
Dekane
Oleic acid
Paraffin
Castor oil
Olive oil
Valeric acid
Carbon tetrachloride
Benzoic aldehyde
Phenyl chloride
Benzoic acid
Ether
Nitrobenzene
Isoamyl alcohol
Toluene
m. Toluidine
Stannic chloride
Acetophenone
Hexane
Triethylamine
Isobutyl isobutyrate
Dekane
Oleic acid
Paraffin
Castor oil
Olive oil

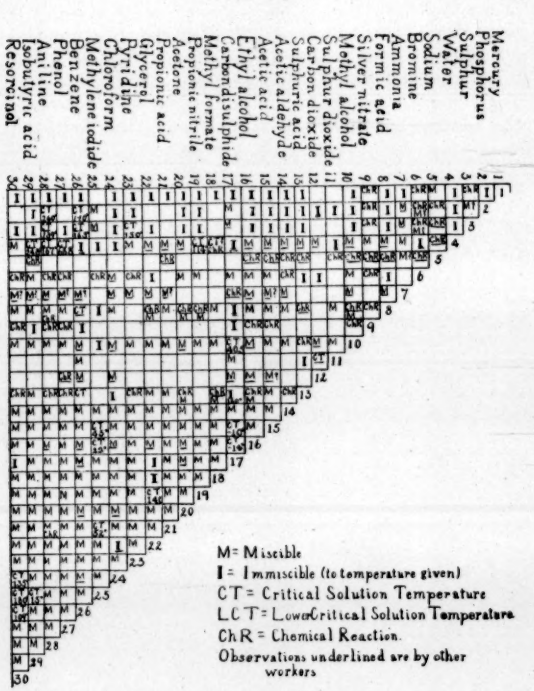


Table of Miscibilities
of
Pairs of Substances
in the
Liquid State.

Beilstein's "Handbuch." The results for ammonia were taken from the work of Franklin and Kraus,[1] and those for carbon dioxide from the work of Büchner.[2]

DISCUSSION OF RESULTS.

The substances in the table, as stated above, have been arranged in the order of their molecular volumes, at the ordinary temperature, 20°, or at the melting point of the higher melting substance in case one or both of the substances are solid at the ordinary temperature. For various reasons it seemed to the author that this grouping might bring out some useful relations. Others have suggested association and dielectric constant as a basis of comparison. As a matter of fact the results do not differ so very widely whichever of these is made the basis of comparison, *i. e.*, the substances having large dielectric constants and high association are also, in general, substances of small molecular volume.

This arrangement causes most of the immiscible pairs to lie in the upper part, and especially the upper left of the table. In other words, substances of very small molecular volume, when mixed with other substances of larger molecular volume, are often immiscible with them. Water illustrates this fact admirably, for if it is brought into contact with various series of organic compounds, the solubility continually decreases as the molecular volume of the latter increases. With methyl alcohol, mol. vol. = 39.5, ethyl alcohol, mol. vol. = 57.9, and propyl alcohol, mol. vol. = 74.7, water is completely miscible. With secondary butyl alcohol, mol. vol. = 89.5, isobutyl alcohol, mol. vol. = 92.3, and isoamyl alcohol, mol. vol. = 105.5, water has a critical solution temperature. With the higher alcohols water is immiscible so far as I have been able to ascertain. Again, with formic acid, mol. vol. = 37.7, acetic acid, mol. vol. = 57.0 and propionic acid, mol. vol. = 74.3, water is completely miscible, but with butyric acid, mol. vol. = 91.7 and isobutyric acid, mol. vol. = 92.6, water has a critical solution temperature, while with valeric acid,

[1] THIS JOURNAL, **24**, 83 (1900).
[2] Z. physik. Chem., **54**, 665 (1906).

mol. vol. = 93.6, and the higher acids it is immiscible so far as ascertained. Moreover, of the 2 isomeric butyric acids the one with the smaller molecular volume is miscible at the lower temperature.

This comparison may be extended to other series—aldehydes, ketones and nitriles, but it is not necessary to pursue this line further at present.

Exceptions to the observation in the preceding paragraph occur, of course, in case the 2 components unite chemically. Thus bromine and sulphur can hardly be said to be miscible since there is evidently a union between them. So stannic chloride and water unite to form, not a mere physical mixture, but a chemical union, as evidenced by the great affinity between them and by the resulting hydrates which are formed.

It has been remarked that the immiscible pairs occur, for the most part, at the left of the table. If the first 10 substances are eliminated and thus the first 10 rows of the table, the remaining pairs are principally miscible at some temperature attained in the present series of experiments. The exceptions are noteworthy; they are nearly all pairs containing, as 1 component, sulphuric acid, glycerol, or stannic chloride. These substances, so markedly diverse in most properties, have yet one property in common, *i. e.*, a great affinity for water. Furthermore, the substances with which they are immiscible, as given in the table, are those materials which dissolve water very sparingly. With sulphuric acid the following substances are immiscible: sulphur dioxide, carbon disulphide, chloroform, toluene, hexane and dekane. Wiih stannic chloride are immiscible chloroform, methylene iotdde, benzene, carbon tetrachloride, toluene, hexane, dekane, oleic acid and paraffin. With glycerol are immiscible carbon disulphide, methyl formate, chloroform, phenyl chloride, ether, carbon tetrachloride, nitrobenzene, toluene, *m*-toluidine, acetophenone, hexane, triethylamine, isobutyl isobutyrate, dekane and oleic acid. It should be noted that no substance which is miscible with water is immiscible with sulphuric acid, stannic chloride, or glycerol. Moreover, many substances, in which water is only moderately soluble, are miscible with all

3 of these in the state of dehydration in which I obtained and used them.

The explanation of these exceptions would seem, then, to be incomplete dehydration. Propionic nitrile offers an interesting case in support of this explanation. Propionic nitrile and water have a critical solution temperature. Propionic nitrile and glycerol are immiscible at ordinary temperatures, hence they should mix at a somewhat elevated temperature if the above explanation is correct. As a matter of fact, they were found to become miscible at 140°.

An effort was made to dehydrate the glycerol by means of anhydrous copper sulphate in sealed tubes, heated and agitated for many weeks. This effort showed the presence of moisture by the hydration of the copper sulphate but the dehydration was evidently incomplete.

It may be asked why these substances, manifestly containing some water, were included in this table? The answer is, merely to be absolutely impartial in the choice of representative liquids as to all properties, of molecular weight, specific gravity, melting point, composition, association, dielectric constant, and it may now be shown that these results are not without interest in the light of other facts, because certain solubility data in the literature are quite contradictory as given in different places. These discrepancies may be partly explained by the above experiments. For example, it has been recorded that carbon disulphide is immiscible with ethyl alcohol. Rothmund showed that they are miscible, if pure, down to —14°. A slight amount of water present in the alcohol prevents miscibility.

Rothmund recorded that benzene and hexane form an immiscible pair. I have found them miscible to the lowest temperatures obtained with a freezing mixture. The data for benzene and chloroform seem contradictory as recorded by Watts and by Beilstein. I have noted that acetone and isobutyl isobutyrate are miscible down to —15° at least, but even on standing for a short time in an open tube, they become immiscible.

The above considerations lead me, therefore, to suggest the

possible use of substances in which water is very sparingly soluble, such as ligroin, melted paraffin, or carbon disulphide to test the dehydration of organic liquids and easily fusible solids. If such substances are completely dehydrated, I believe that all except the first members of the series will be completely miscible. Thus in the table, formic acid and methyl alcohol are immiscible with paraffin. Acetic acid and paraffin are miscible at a somewhat elevated temperature. All the others are miscible at the ordinary temperature. It must be remembered that even after being dried as completely as possible, these contained a trace of water.

There are only 2 remaining exceptions to the entire miscibility of the approximately 700 pairs of substances obtained by combinations of the last 40 substances of the table. These exceptions are carbon disulphide and resorcinol and dekane and resorcinol. Further study will be devoted to these cases and to those pairs which gave critical solution temperatures.

CONCLUSIONS.

1. The miscibility or immiscibility of a large number of pairs of liquids has been tested.

2. It is found that substances of small molecular volume are often immiscible with other substances of large molecular volume.

3. It is pointed out that the presence of small amounts of water may often account for the immiscibility of substances. The possibility of utilizing this fact in obtaining a test for dehydration is suggested.

The author takes especial pleasure in thanking Prof. J. J. Thomson for advice and kindly criticism during the progress of this work and for the free use of the facilities of the Cavendish Laboratory.

CAMBRIDGE, ENGLAND,
July, 1906.

THE OSMOTIC PRESSURE OF GLUCOSE SOLUTIONS IN THE VICINITY OF THE FREEZING POINT OF WATER.[1]

By H. N. Morse, J. C. W. Frazer and F. M. Rogers.

The arrangements by means of which the low temperatures required for the present work were secured and maintained have been described in an earlier communication,[2] in which an account was given of the pressures exerted by cane sugar solutions in the neighborhood of 0°.

The material employed for the measurements, like that used in the first series of determinations with glucose,[3] was "Traubenzucker Kahlbaum." It was, however, distinctly less pure than that which was obtained on the former occasion. After aerating the pulverized substance and allowing it to stand in an exhausted desiccator until it gave no reaction for alcohol, it was found to have a somewhat uncertain melting point of 143°. Four determinations of carbon and hydrogen gave: for the former 40.28, 40.26, 40.35, and 40.35 instead of 39.98 per cent; and for the latter, 6.60, 6.66, 6.62, and 6.69 instead of 6.71 per cent. A solution[4] containing, in 100 cc. at 17°.5, 32.65 grams of the glucose gave a rotation of 101.45 instead of 100, saccharimeter degrees. The excessive rotation of the solutions and the abnormally high percentage of carbon led us to suspect the presence of dextrin, but no reaction for that substance could be obtained with iodine.

The material was then four times recrystallized by precipitating it with alcohol from its aqueous solutions. Thus purified, its melting point was found to be 145°–146°, instead of 146°, and the standard solution gave a rotation of 100.5 instead of 100 saccharimeter degrees. Two analyses gave: For the

[1] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The papers upon the subject which have preceded the present one will be found in this Journal, 26, 80; 28, 1; 29, 173; 32, 93; 34, 1; 36, 1, 39; 37, 324 and 425.

[2] This Journal, 37, 425.

[3] *Ibid.*, 37, 329.

[4] Landolt, "Optische Drehungsvermögen," 448.

carbon, 40.09 and 39.96 instead of 39.98 per cent; and for the hydrogen, 6.64 and 6.77 instead of 6.71 per cent.

The record of the measurements of pressure are given with the customary fulness of detail in the following tables (I.-XX.). The results are stated in two ways, according to the two views which may be held regarding the proper method of correcting the observed pressures for the loss in rotation which the solutions suffer while in the cells. It has been intimated in a former paper[1] that probably *not less* than one-half of the loss in rotation is due to dilution which occurs while the cell is being opened, that is, to dilution which is subsequent to the measurement of the pressure. If this is true, the observed pressures should not be corrected for more than one-half the loss in rotation. In our opinion, the values given in the tables under "*Results, if corrected for one-half the loss in rotation,*" are more nearly correct than those presented under "*Results, if corrected for the whole loss in rotation.*"

With the record of each measurement there are given: 1, the *molecular osmotic pressure, i. e.*, the pressure divided by the weight-normal concentration of the solution; 2, *the ratio of the osmotic to the calculated gas pressure for the same temperature,* the volume of the gas being that of the solvent in the pure state; and 3, the *ratio of the observed molecular depression of the freezing point*[2] (Δ) of each solution to 1.85, the calculated molecular depression of the freezing point of water.

In Tables XXI. to XXV. the more important values recorded in Tables I. to XX. are brought together for greater convenience of comparison.

It will be noted (Table XXI., column 4) that the resistance of the membranes employed in the present series of measurements was greater than that recorded for the same cells in earlier work. The difference is due to the lower temperature at the time of deposition. The maximum resistance which a membrane in a given cell will exhibit is largely a matter of temperature; the lower the temperature is, the higher will be the resistance of the membrane. Of late, it has been our prac-

[1] THIS JOURNAL, 37, 463.
[2] *Ibid.*, 37, 360.

Table I.

Original wt. normal concentration of solution, 0.1.
Rotation of original solution, 5°.22.
Rotation at conclusion of experiment, 5°.20.
Loss in concentration, 0°.02 = 0.38 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 4.00 P.M., March 13, 1907.

Experiment No. 1.
Manometer used, 20.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 546,000.
Initial pressure, 1.43 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 13											
5.00 P.M.	0°.18	3°.70	242.02	238.78							
7.30 "	0°.18	1°.16	184.64	183.85							
11.00 "	0°.15	1°.06	170.17	169.51	0.99	0.43	0.01	0.02	2.39	2.23	0.16
March 14											
9.00 A.M.	0°.26	0°.82	169.40	168.89	1.00	0.43	0.01	0.02	2.39	2.23	0.16
12.30 P.M.	0°.32	0°.99	169.43	168.82	0.99	0.43	0.01	0.02	2.40	2.23	0.17
3.30 "	0°.38	1°.13	169.41	168.71	0.99	0.43	0.01	0.02	2.40	2.23	0.17
	0°.28										

Displacement of the manometer = 0.04 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.01 atmosphere.
Osmotic pressure = 2.40 atmospheres.
Molecular pressure = 23.95 atmospheres.
Ratio of osmotic to gas pressure = 1.074.

Results, if corrected for half the loss in rotation:
Correction = 0.005 atmosphere.
Osmotic pressure = 2.39 atmospheres.
Molecular pressure = 23.90 atmospheres.
Ratio of osmotic to gas pressure = 1.071.
Ratio of Δ to 1.85 = 1.038.

Table II.

Original wt. normal concentration of solution, 0.1.
Rotation of original solution, 5°.22.
Rotation at conclusion of experiment, 5°.22.
Loss in concentration, 0°.00.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 3.30 P.M., March 14, 1907.

Experiment No. 2.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 550,000.
Initial pressure, 2.13 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 14											
5.00 P.M.	0°.22	4°.80	176.62								
7.45 "	0°.20	0°.87	163.50								
11.15 "	0°.18	0°.69	159.08	158.68	1.00	0.37	0.00	0.02	2.40	2.23	0.17
March 15											
10.00 A.M.	0°.24	0°.57	158.43	158.10	1.01	0.37	0.00	0.02	2.40	2.23	0.17
12.30 P.M.	0°.25	0°.63	158.44	158.07	1.01	0.37	0.00	0.02	2.40	2.23	0.17
4.15 "	0°.28	0°.77	158.47	158.02	1.01	0.37	0.00	0.02	2.41	2.23	0.17
	0°.24										

Displacement of manometer = 0.17 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.00.
Osmotic pressure = 2.40 atmospheres.
Molecular pressure = 24.03 atmospheres.
Ratio of osmotic to gas pressure = 1.077.

Results, if corrected for half the loss in rotation:
Correction = 0.00.
Osmotic pressure = 2.40 atmospheres.
Molecular pressure = 24.03 atmospheres.
Ratio of osmotic to gas pressure = 1.077.
Ratio of Δ to 1.85 = 1.038.

Table III.

Original wt. normal concentration of solution, 0.2.
Rotation of original solution, 10°.4.
Rotation at conclusion of experiment, 10°.3.
Loss in concentration, 0°.1 = 0.96 per cent.
Calibration units of air in manometer, 396.89.
Time of setting up cell, 4.30 P.M., Feb. 15, 1907.

Experiment No. 1.
Manometer used, No. 6.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 543,000.
Initial pressure, 4.30 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 15											
6.00 P.M.	0°.12	1°.40	85.08								
9.00 "	0°.10	0°.79	79.87	79.64	1.00	0.60	0.05	0.02	4.65	4.45	0.20
11.30 "	0°.12	0°.72	79.75	79.54	1.00	0.60	0.05	0.02	4.66	4.45	0.21
Feb. 16											
8.30 A.M.	0°.12	0°.64	79.71	79.52	1.00	0.60	0.05	0.02	4.66	4.45	0.21
11.30 "	0°.12	0°.79	79.75	79.52	1.00	0.60	0.05	0.02	4.66	4.45	0.21
	0°.12										

Displacement of manometer = 0.05 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.05 atmosphere.
Osmotic pressure = 4.66 atmospheres.
Molecular pressure = 23.29 atmospheres.
Ratio of osmotic to gas pressure = 1.047.

Results, if corrected for half the loss in rotation:
Correction = 0.025 atmosphere.
Osmotic pressure = 4.64 atmospheres.
Molecular pressure = 23.16 atmospheres.
Ratio of osmotic to gas pressure = 1.041.
Ratio of Δ to 1.85 = 1.038.

Table IV.

Original wt. normal concentration of solution, 0.2
Rotation of original solution, 10°.50.
Rotation at conclusion of experiment, 10°.45.
Loss in concentration, 0°.05 = 0.48 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 3.45 P.M., Feb. 19, 1907.

Experiment No. 2.
Manometer used, No. 20.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 502,500.
Initial pressure, 4.07 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 19											
5.45 P.M.	0°.12	2°.60	110.03	108.99							
8.00 "	0°.12	0°.96	98.08	97.73							
11.00 "	0°.12	0°.87	97.44	97.13	0.99	0.52	0.03	0.02	4.68	4.45	0.23
Feb. 20											
10.00 A.M.	0°.14	0°.75	97.48	97.21	0.99	0.52	0.03	0.02	4.67	4.45	0.22
1.00 P.M.	0°.14	0°.75	97.43	97.16	0.99	0.52	0.03	0.02	4.68	4.45	0.23
4.15 "	0°.12	0°.79	97.45	97.17	0.99	0.52	0.03	0.02	4.68	4.45	0.23
	0°.13										

Displacement of manometer = 0.04 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.03 atmosphere.
Osmotic pressure = 4.68 atmospheres.
Molecular pressure = 23.39 atmospheres.
Ratio of osmotic to gas pressure = 1.051.

Results, if corrected for half the loss in rotation:
Correction = 0.015 atmosphere.
Osmotic pressure = 4.66 atmospheres.
Molecular pressure = 23.31 atmospheres.
Ratio of osmotic to gas pressure = 1.048.
Ratio of Δ to 1.85 = 1.038.

Table V.

Original wt. normal concentration of solution, 0.3.
Rotation of original solution, 15°.65.
Rotation at conclusion of experiment, 15°.55.
Loss in concentration, 0°.10 = 0.64 per cent.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 12.30 P.M., Feb. 16, 1907.

Experiment No. 1.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 505,000.
Initial pressure, 5.91 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 16											
1.15 P.M.	0°.15	2°.80	75.31	74.54							
5.30 "	0°.16	0°.96	64.37	64.14	0.99	0.50	0.05	0.02	7.03	6.68	0.35
8.00 "	0°.17	0°.98	64.31	64.08	0.99	0.50	0.05	0.02	7.04	6.68	0.36
11.45 "	0°.18	0°.94	64.28	64.06	0.99	0.50	0.05	0.02	7.04	6.68	0.36
Feb. 17											
9.30 A.M.	0°.24	0°.98	64.29	64.06	0.99	0.50	0.05	0.02	7.04	6.68	0.36
	0°.19										

Displacement of manometer = 0.16 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.05 atmosphere.
Osmotic pressure = 7.04 atmospheres.
Molecular pressure = 23.45 atmospheres.
Ratio of osmotic to gas pressure = 1.054.

Results, if corrected for half the loss in rotation:
Correction = 0.025 atmosphere.
Osmotic pressure = 7.01 atmospheres.
Molecular pressure = 23.38 atmospheres.
Ratio of osmotic to gas pressure = 1.050.
Ratio of Δ to 1.85 = 1.038.

DUPONT COMPANY
EXPERIMENTAL STATION
LIBRARY.

Table VI.

Original wt. normal concentration of solution, 0.3.
Rotation of original solution, 15°.53.
Rotation at conclusion of experiment, 15°.42.
Loss in concentration, 0°.11 = 0.71 per cent.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 3.45 P.M., March 18, 1907.

Experiment No. 2.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 368,000.
Initial pressure, 5.83 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.			
March 18											
4.45 P.M.	0°.18	5°.00	76.96	75.57							
8.00 "	0°.17	0°.69	64.18	64.02	1.01	0.50	0.06	0.02	7.04	6.68	0.36
11.00 "	0°.18	0°.60	64.15	64.01	1.01	0.50	0.06	0.02	7.04	6.68	0.36
March 19											
10.15 A.M.	0°.23	0°.55	64.18	64.05	1.00	0.50	0.06	0.02	7.05	6.68	0.37
12.30 P.M.	0°.25	0°.55	64.20	64.07	1.00	0.50	0.06	0.02	7.04	6.69	0.35
3.00 "	0°.26	0°.60	64.20	64.06	0.99	0.50	0.06	0.02	7.05	6.69	0.36
	0°.25										

Displacement of manometer = 0.15 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.06 atmosphere.
Osmotic pressure = 7.04 atmospheres.
Molecular pressure = 23.48 atmospheres.
Ratio of osmotic to gas pressure = 1.054.

Results, if corrected for half the loss in rotation:
Correction = 0.03 atmosphere.
Osmotic pressure = 7.01 atmospheres.
Molecular pressure = 23.38 atmospheres.
Ratio of osmotic to gas pressure = 1.049.
Ratio of i to 1.85 = 1.038.

Table VII.

Original wt. normal concentration of solution, 0.4.
Rotation of original solution, 20°.65.
Rotation at conclusion of experiment, 20°.50.
Loss in concentration, 0°.15 = 0.73 per cent.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 4.30 P.M., Feb. 18, 1907.

Experiment No. 1.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 434,000.
Initial pressure, 9.09 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 18											
6.00 P.M.	0°.14	2°.00	50.46	50.09							
8.00 "	0°.12	0°.91	49.26	49.09	1.00	0.52	0.08	0.02	9.36	8.91	0.45
11.15 "	0°.12	0°.76	49.23	49.09	1.00	0.52	0.08	0.02	9.36	8.91	0.45
Feb. 19											
10.15 A.M.	0°.12	0°.72	49.41	49.27	0.99	0.52	0.08	0.02	9.33	8.91	0.42
12.45 P.M.	0°.12	0°.80	49.38	49.23	0.98	0.52	0.08	0.02	9.35	8.91	0.44
4.00 "	0°.14	0°.93	49.44	49.27	0.98	0.52	0.08	0.02	9.34	8.91	0.43
	0°.13										

Displacement of manometer = 0.00.

Results, if corrected for whole loss in rotation:
Correction = 0.08 atmosphere.
Osmotic pressure = 9.35 atmospheres.
Molecular pressure = 23.37 atmospheres.
Ratio of osmotic to gas pressure = 1.049.

Results, if corrected for half the loss in rotation:
Correction = 0.04 atmosphere.
Osmotic pressure = 9.31 atmospheres.
Molecular pressure = 23.27 atmospheres.
Ratio of osmotic to gas pressure = 1.045.
Ratio of Δ to 1.85 = 1.038.

Table VIII.[a]

Original wt. normal concentration of solution, 0.4.
Rotation of original solution, 20°.58.
Rotation at conclusion of experiment, 20°.40.
Loss in concentration, 0°.18 = 0°.87 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 4.00 P.M., March 15, 1907.

Experiment No. 2.
Manometer used, No. 20.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 360,000.
Initial pressure, 7.25 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 15											
5.15 P.M.	0°.22	4°.60	65.69	64.59							
7.30 "	0°.20	0°.80	51.98	51.83							
11.00 "	0°.19	0°.69	51.46	51.33	1.01	0.58	0.09	0.02	9.33	8.91	0.42
March 16											
8.45 A.M.	0°.14	0°.54	51.39	51.29	1.01	0.58	0.09	0.02	9.33	8.91	0.42
5.00 P.M.	0°.30	0°.72	51.46	51.32	1.01	0.58	0.09	0.02	9.33	8.92	0.41
	0°.21		Displacement of manometer = 0.34 mm.								

Results, if corrected for whole loss in rotation:
Correction = 0.09 atmosphere.
Osmotic pressure = 9.33 atmospheres.
Molecular pressure = 23.33 atmospheres.
Ratio of osmotic to gas pressure = 1.047.

Results, if corrected for half the loss in rotation:
Correction = 0.045 atmosphere.
Osmotic pressure = 9.29 atmospheres.
Molecular pressure = 23.21 atmospheres.
Ratio of osmotic to gas pressure = 1.042.
Ratio of Δ to 1.85 = 1.038.

Table IX.

Original wt. normal concentration of solution, 0.5.
Rotation of original solution, 25°.55.
Rotation at conclusion of experiment, 25°.40.
Loss in concentration, 0.°15 = 0.58 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 4.15 P.M., Mar. 11, 1907.

Experiment No. 1.
Manometer used, No 20.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 564,000.
Initial pressure, 10.00 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 11											
5.15 P.M.	0°.24	2°.30	48.10	47.70							
8.00 "	0°.17	0°.94	41.40	41.26	1.01	0.60	0.07	0.02	11.68	11.14	0.54
11.45 "	0°.12	0°.85	41.32	41.19	1.01	0.60	0.07	0.02	11.70	11.14	0.56
March 12											
10.00 A.M.	0°.17	0°.72	41.35	41.24	1.01	0.60	0.07	0.02	11.69	11.14	0.55
12.45 P.M.	0°.19	0°.86	41.35	41.21	1.00	0.60	0.07	0.02	11.70	11.14	0.56
3.30 "	0°.18	0°.94	41.36	41.22	1.00	0.60	0.07	0.02	11.70	11.14	0.56
	0°.17										

Displacement of manometer = 0.18 mm.

Results, if corrected for whole loss in rotation:
Correction =0.07 atmosphere.
Osmotic pressure = 11.69 atmospheres.
Molecular pressure = 23.39 atmospheres.
Ratio of osmotic to gas pressure = 1.050.

Results, if corrected for half the loss in rotation:
Correction = 0.035 atmosphere.
Osmotic pressure = 11.66 atmospheres.
Molecular pressure = 23.32 atmospheres.
Ratio of osmotic to gas pressure = 1.047.
Ratio of Δ to 1.85 = 1.038.

Table X.

Original wt. normal concentration of solution, 0.5.
Rotation of original solution, 25°.55.
Rotation at conclusion of experiment, 25°.30.
Loss in concentration, 0°.25 = 0.98 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 4.00 P.M., Mar. 19, 1907.

Experiment No. 2.
Manometer used, No. 20.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 370,000.
Initial pressure, 9.82 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 19											
5.00 P.M.	0°.19	2°.60	48.97	48.51							
7.30 "	0°.14	0°.74	41.75	41.64							
11.00 "	0°.14	0°.71	41.57	41.46	0.98	0.60	0.12	0.02	11.70	11.14	0.56
March 20											
10.00 A.M.	0°.24	0°.57	41.59	41.50	0.99	0.60	0.12	0.02	11.68	11.14	0.54
1.00 P.M.	0°.27	0°.64	41.54	41.44	0.99	0.60	0.12	0.02	11.70	11.14	0.56
3.30 "	0°.29	0°.71	41.59	41.48	1.00	0.60	0.12	0.02	11.67	11.14	0.55
	0°.24										

Displacement of manometer = 0.06 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.12 atmosphere.
Osmotic pressure = 11.69 atmospheres.
Molecular pressure = 23.38 atmospheres.
Ratio of osmotic to gas pressure = 1.049.

Results, if corrected for half the loss in rotation:
Correcton = 0.06 atmosphere.
Osmotic pressure = 11.63 atmospheres.
Molecular pressure = 23.26 atmospheres.
Ratio of osmotic to gas pressure = 1.044.
Ratio of Δ to 1.85 = 1.038.

Table XI.

Original wt. normal concentration of solution, 0.6.
Rotation of original solution, 30°.65.
Rotation at conclusion of experiment, 30°.10.
Loss in concentration, 0°.55 = 1.47 per cent.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 4.00 P.M., Feb. 20, 1907.

Experiment No. 1.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, B.
Resistance of membrane, 547,000.
Initial pressure, 12.93 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 20											
5.30 P.M.	0°.12	1°.60	35.96	35.75							
7.30 "	0°.10	0°.86	33.58	33.47							
11.15 "	0°.08	0°.79	33.45	33.35	0.99	0.54	0.22	0.02	14.13	13.36	0.77
Feb. 21											
10.15 A.M.	0°.12	0°.72	33.52	33.43	0.99	0.54	0.22	0.02	14.09	13.36	0.73
1.00 P.M.	0°.14	0°.79	33.47	33.37	0.99	0.54	0.22	0.02	14.12	13.36	0.76
4.30 "	0°.14	0°.73	33.46	33.37	0.99	0.54	0.22	0.02	14.12	13.36	0.76
	0°.12										

Displacement of manometer = 0.06 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.22 atmosphere.
Osmotic pressure = 14.12 atmospheres.
Molecular pressure = 23.53 atmospheres.
Ratio of osmotic to gas pressure = 1.057.

Results, if corrected for half the loss in rotation:
Correction = 0.11 atmosphere.
Osmotic pressure = 14.01 atmospheres.
Molecular pressure = 23.34 atmospheres.
Ratio of osmotic to gas pressure = 1.048.
Ratio of Δ to 1.85 = 1.038.

Table XII.

Original wt. normal concentration of solution, 0.6. Experiment No. 2.
Rotation of original solution, 30°.55. Manometer used, No. 21.
Rotation at conclusion of experiment, 30°.10 Capillary depression, 0.02.
Loss in concentration, 0°.45 = 1.47 per cent. Cell used, G.
Calibration units of air in manometer, 478.16. Resistance of membrane, 545,000.
Time of setting up cell, 4.15 P.M., Feb. 22, 1907. Initial pressure, 13.64 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 22											
5.30 P.M.	**0°.06**	**1°.40**	**34.17**	**33.96**							
8.00 "	0°.08	0°.49	33.37	33.31	1.02	0.54	0.22	0.02	14.11	13.36	0.78
11.30 "	0°.08	0°.43	33.30	33.25	1.02	0.54	0.22	0.02	14.14	13.36	0.75
Feb. 23											
10.30 A.M.	0°.08	0°.39	33.33	33.28	1.03	0.54	0.22	0.02	14.11	13.36	0.75
1.00 P.M.	0°.08	0°.46	33.36	33.30	1.02	0.54	0.22	0.02	14.11	13.36	0.75
4.30 "	0°.08	0°.50	33.36	33.30	1.02	0.54	0.22	0.02	14.11	13.36	0.75
	0°.08										

Displacement of manometer = 0.00.

Results, if corrected for whole loss in rotation:
Correction = 0.22 atmosphere.
Osmotic pressure = 14.12 atmospheres.
Molecular pressure = 23.53 atmospheres
Ratio of osmotic to gas pressure = 1.057.

Results, if corrected for half the loss in rotation:
Correction = 0.11 atmosphere.
Osmotic pressure = 14.01 atmospheres.
Molecular pressure = 23.34 atmospheres.
Ratio of osmotic to gas pressure = 1.048.
Ratio of Δ to 1.85 = 1.038.

Table XIII.

Original wt. normal concentration of solution, 0.7.
Rotation of original solution, 35°.30.
Rotation at conclusion of experiment, 34°.95..
Loss in concentration, 0°.35 = 0.99 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 4.30 P.M., Feb. 21, 1907.

Experiment No. 1.
Manometer used, No. 20.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 364,000.
Initial pressure, 15.68 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 21											
5.45 P.M.	0°.12	2°.00	31.07	30.84							
8.00 "	0°.10	0°.70	29.93	29.85							
Feb. 22											
12.45 A.M.	0°.10	0°.55	29.79	29.73	1.00	0.61	0.17	0.02	16.45	15.59	0.86
9.00 "	0°.06	0°.43	29.80	29.75	1.01	0.61	0.17	0.02	16.43	15.59	0.84
1.00 P.M.	0°.08	0°.43	29.79	29.74	1.01	0.61	0.17	0.02	16.44	15.59	0.85
4.00 "	0°.08	0°.49	29.77	29.72	1.01	0.61	0.17	0.02	16.45	15.59	0.86
	0°.08										

Displacement of manometer = 0.12 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.17 atmosphere.
Osmotic pressure = 16.44 atmospheres.
Molecular pressure = 23.49 atmospheres.
Ratio of osmotic to gas pressure = 1.055.

Results, if corrected for half the loss in rotation:
Correction = 0.085 atmosphere.
Osmotic pressure = 16.36 atmospheres.
Molecular pressure = 23.37 atmospheres.
Ratio of osmotic to gas pressure = 1.049.
Ratio of d to 1.85 = 1.038.

Table XIV.

Original wt. normal concentration of solution, 0.7.
Rotation of original solution, 35°.25.
Rotation at conclusion of experiment, 35°.05.
Loss in concentration, 0°.20 = 0.57 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 5.30 P.M., Feb. 23, 1907.

Experiment No. 2.
Manometer used, No. 20.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 365,000.
Initial pressure, 15.54 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 23											
6.30 P.M.	0°.06	0°.85	31.18	31.08							
8.15 "	0°.07	0°.59	29.75	29.69							
12.00 "	0°.06	0°.51	29.68	29.62	1.02	0.61	0.10	0.02	16.42	15.59	0.83
Feb. 24											
10.15 A.M.	0°.06	0°.48	29.66	29.61	1.02	0.61	0.10	0.02	16.42	15.59	0.83
	0°.06		Displacement of manometer = 0.00.								

Results, if corrected for whole loss in rotation:
Correction = 0.10 atmosphere.
Osmotic pressure = 16.42 atmospheres.
Molecular pressure = 23.46 atmospheres.
Ratio of osmotic to gas pressure = 1.053.

Results, if corrected for half the loss in rotation:
Correction = 0.05 atmosphere.
Osmotic pressure = 16.37 atmospheres.
Molecular pressure = 23.39 atmospheres.
Ratio of osmotic to gas pressure = 1.050.
Ratio of Δ to 1.85 = 1.038.

Table XV.

Original wt. normal concentration of solution, 0.8.
Rotation of original solution, 39°.85.
Rotation at conclusion of experiment, 39°.40.
Loss in concentration, 0°.45 = 1.13 per cent.
Calibration units of air in manometer, 495.09.
Time of setting up cell, 3.45 P.M., Feb. 26, 1907.

Experiment No. 1.
Manometer used, No. 20.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 550,000.
Initial pressure, 17.52 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 26											
5.00 P.M.	0°.12	2°.60	27.93	27.68							
8.00 "	0°.12	0°.73	26.18	26.11							
11.00 "	0°.12	0°.70	26.15	26.08	1.00	0.62	0.22	0.02	18.84	17.82	1.02
Feb. 27											
10.00 A.M.	0°.12	0°.75	26.15	26.08	1.00	0.62	0.22	0.02	18.84	17.82	1.02
1.00 P.M.	0°.15	0°.83	26.13	26.05	1.00	0.62	0.22	0.02	18.87	17.82	1.05
4.00 "	0°.14	0°.83	26.11	26.03	1.01	0.62	0.22	0.02	18.87	17.82	1.05
	0°.13		Displacement of manometer = 0.20 mm.								

Results, if corrected for whole loss in rotation:
Correction = 0.22 atmosphere.
Osmotic pressure = 18.86 atmospheres.
Molecular pressure = 23.57 atmospheres.
Ratio of osmotic to gas pressure = 1.058.

Results, if corrected for half the loss in rotation:
Correction = 0.11 atmosphere.
Osmotic pressure = 18.75 atmospheres.
Molecular pressure = 23.43 atmospheres.
Ratio of osmotic to gas pressure = 1.052.
Ratio of Δ to 1.85 = 1.038.

Table XVI.

Original wt. normal concentration of solution, 0.8.
Rotation of original solution, 39°.85.
Rotation at conclusion of experiment, 39°.50.
Loss in concentration, 0°.35 = 0.88 per cent.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 4.00 P.M., Feb. 26, 1907.

Experiment No. 2.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 367,000.
Initial pressure, 17.36 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 26											
5.00 P.M.	0°.12	2°.60	27.12	26.88							
8.00 "	0°.12	0°.73	25.10	25.03	1.00	0.55	0.17	0.02	18.84	17.82	1.02
11.00 "	0°.12	0°.70	25.02	24.96	1.00	0.55	0.17	0.02	18.90	17.82	1.08
Feb. 27											
10.00 A.M.	0°.12	0°.75	25.08	25.01	1.00	0.55	0.17	0.02	18.86	17.82	1.04
1.00 P.M.	0°.15	0°.83	25.10	25.02	1.00	0.55	0.17	0.02	18.85	17.82	1.03
4.00 "	0°.14	0°.83	25.09	25.01	1.01	0.55	0.17	0.02	18.85	17.82	1.03
	0°.13										

Displacement of manometer = 0.05. mm.

Results, if corrected for whole loss in rotation:
Correction = 0.17 atmosphere.
Osmotic pressure = 18.86 atmospheres.
Molecular pressure = 23.58 atmospheres.
Ratio of osmotic to gas pressure = 1.058.

Results, if corrected for half the loss in rotation:
Correction = 0.085 atmosphere.
Osmotic pressure = 17.78 atmospheres.
Molecular pressure = 23.47 atmospheres.
Ratio of osmotic to gas pressure = 1.054.
Ratio of d to 1.85 = 1.038.

Table XVII.

Original wt. normal concentration of solution, 0.9. Experiment No. 1.
Rotation of original solution, 44°.40. Manometer used, No. 20.
Rotation at conclusion of experiment, 43°.70. Capillary depression, 0.02.
Loss in concentration, 0°.70 = 1.58 per cent. Cell used, G.
Calibration units of air in manometer, 495.09. Resistance of membrane, 560,000.
Time of setting up cell, 3.45 P.M., March 1, 1907. Initial pressure, 19.55 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.			
March 1											
5.00 P.M.	0°.12	3°.50	25.19	24.87							
7.30 "	0°.12	0°.78	23.28	23.21							
11.00 "	0°.10	0°.73	23.24	23.18	1.00	0.62	0.35	0.02	21.35	20.05	1.30
March 2											
10.30 A.M.	0°.14	0°.86	23.25	23.18	0.99	0.62	0.35	0.02	21.36	20.05	1.31
12.45 P.M.	0°.16	1°.05	23.26	23.17	0.99	0.62	0.35	0.02	21.37	20.05	1.32
5.00 "	0°.24	1°.10	23.25	23.16	0.99	0.62	0.35	0.02	21.38	20.05	1.33
	0°.16		Displacement of manometer = 0.15 mm.								

Results, if corrected for whole loss in rotation:
Correction = 0.35 atmosphere.
Osmotic pressure = 21.37 atmospheres.
Molecular pressure = 23.74 atmospheres.
Ratio of osmotic to gas pressure = 1.066.

Results, if corrected for half the loss in rotation:
Correction = 0.175 atmosphere.
Osmotic pressure = 21.19 atmospheres.
Molecular pressure = 23.54 atmospheres.
Ratio of osmotic to gas pressure = 1.057.
Ratio of Δ to 1.85 = 1.038.

Table XVIII.

Original wt. normal concentration of solution, 0.9.
Rotation of original solution, 44°.40.
Rotation at conclusion of experiment, 44°.00.
Loss in concentration, 0°.40 = 0.91 per cent.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 4.00 P.M. March 1, 1907.

Experiment No. 2.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 555,000.
Initial pressure, 20.77 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 1											
5.00 P.M.	0°.12	3°.50	23.98	23.68							
7.30 "	0°.12	0°.78	22.20	22.14	1.00	0.56	0.20	0.02	21.38	20.05	1.33
11.00 "	0°.10	0°.73	22.14	22.08	1.00	0.56	0.20	0.02	21.44	20.05	1.39
March 2											
10.45 A.M.	0°.14	0°.86	22.18	22.11	0.99	0.56	0.20	0.02	21.41	20.05	1.36
12.45 P.M.	0°.16	1°.05	22.24	22.15	0.99	0.56	0.20	0.02	21.38	20.05	1.33
5.00 "	0°.24	1°.10	22.24	22.15	0.99	0.56	0.20	0.02	21.38	20.05	1.33
	0°.15										

Displacement of manometer = 0.02 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.20 atmosphere.
Osmotic pressure = 21.40 atmospheres.
Molecular pressure = 23.75 atmospheres.
Ratio of osmotic to gas pressure = 1.067.

Results, if corrected for half the loss in rotation:
Correction = 0.10 atmosphere.
Osmotic pressure = 21.30 atmospheres.
Molecular pressure = 23.66 atmospheres.
Ratio of osmotic to gas pressure = 1.062.
Ratio of Δ to 1.85 = 1.038.

Table XIX.

Original wt. normal concentration of solution, 1.0. Experiment No. 1.
Rotation of original solution, 48°.90. Manometer used, No. 20.
Rotation at conclusion of experiment, 48°.20. Capillary depression, 0.02.
Loss in concentration, 0°.70 = 1.43 per cent. Cell used, D.
Calibration units of air in manometer, 495.09. Resistance of membrane, 540,000.
Time of setting up cell, 3.35 P.M., March 4, 1907. Initial pressure, 22.33 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 4											
6.00 P.M.	0°.17	2°.40	22.01	21.82							
11.00 "	0°.12	0°.74	20.87	20.82	1.00	0.62	0.34	0.02	23.76	22.27	1.49
March 5											
8.50 A.M.	0°.16	0°.73	20.87	20.82	1.00	0.62	0.34	0.02	23.76	22.28	1.48
12.45 P.M.	0°.18	0°.90	20.88	20.81	1.00	0.62	0.34	0.02	23.77	22.28	1.49
4.15 "	0°.22	1°.07	20.90	20.82	0.99	0.62	0.34	0.02	23.77	22.28	1.49
	0°.17										

Displacement of manometer = 0.15 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.34 atmosphere.
Osmotic pressure = 23.77 atmospheres.
Molecular pressure = 23.77 atmospheres.
Ratio of osmotic to gas pressure = 1.067.

Results, if corrected for half the loss in rotation:
Correction = 0.17 atmosphere.
Osmotic pressure = 23.60 atmospheres.
Molecular pressure = 23.60 atmospheres.
Ratio of osmotic to gas pressure = 1.059.
Ratio of d to 1.85 = 1.038.

Table XX.

Original wt. normal concentration of solution, 1.0.
Rotation of original solution, 48°.90.
Rotation at conclusion of experiment, 48°.32.
Loss in concentration, 0°.58 = 1.20 per cent.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 4.15 P.M., March 4, 1907.

Experiment No. 2.
Manometer used, No. 21.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 540,000.
Initial pressure, 22.95 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between found and calculated.
March 4											
6.00 P.M.	0°.17	2°.40	20.64	20.46							
11.30 "	0°.12	0°.74	20.06	20.01	1.00	0.56	0.30	0.02	23.78	22.27	1.51
March 5											
10.00 A.M.	0°.16	0°.85	20.11	20.05	1.00	0.56	0.30	0.02	23.73	22.28	1.45
12.45 P.M.	0°.18	0°.90	20.18	20.11	1.00	0.56	0.30	0.02	23.66	22.28	1.38
4.15 "	0°.22	1°.07	20.17	20.09	0.99	0.56	0.30	0.02	23.69	22.28	1.41
	0°.17										

Displacement of manometer = 0.09 mm.

Results, if corrected for whole loss in rotation:
Correction = 0.30 atmosphere.
Osmotic pressure = 23.72 atmospheres.
Molecular pressure = 23.72 atmospheres.
Ratio of osmotic to gas pressure = 1.064.

Results, if corrected for half the loss in rotation:
Correction = 0.15 atmosphere.
Osmotic pressure = 23.57 atmospheres.
Molecular pressure = 23.57 atmospheres.
Ratio of osmotic to gas pressure = 1.055.
Ratio of d to 1.85 = 1.038.

Table XXI.

Weight normal concentration.	No. of experiment.	Cell used.	Resistance of the membrane. Ohms.	Displacement of the manometer. mm.	Loss in rotation. Degree.	Loss in rotation. Per cent.	Pressure equivalent of loss in rotation. Atmosphere.
1	2	3	4	5	6	7	8
0.1	1	D	546,000	0.04	0.02	0.38	0.01
"	2	G	550,000	0.17	0.00	0.00	0.00
0.2	1	G	543,000	0.05	0.10	0.96	0.05
"	2	D	502,500	0.04	0.05	0.48	0.03
0.3	1	D	505,000	0.16	0.10	0.64	0.05
"	2	G	368,000	0.15	0.11	0.71	0.06
0.4	1	G	434,000	0.00	0.15	0.73	0.08
"	2	D	360,000	0.34	0.18	0.87	0.09
0.5	1	D	564,000	0.18	0.15	0.58	0.07
"	2	D	370,000	0.06	0.25	0.98	0.12
0.6	1	B	547,000	0.06	0.55	1.47	0.22
"	2	G	545,000	0.00	0.45	1.47	0.22
0.7	1	D	364,000	0.12	0.35	0.99	0.17
"	2	D	365,000	0.00	0.20	0.57	0.10
0.8	1	G	550,000	0.20	0.45	1.13	0.22
"	2	D	367,000	0.05	0.35	0.88	0.17
0.9	1	G	560,000	0.15	0.70	1.58	0.35
"	2	D	555,000	0.02	0.40	0.91	0.20
1.0	1	D	540,000	0.15	0.70	1.43	0.34
"	2	G	540,000	0.09	0.58	1.20	0.30
						0.90	

tice to deposit the greater portion of the membrane at room temperature, and to complete the operation at whatever temperature the measurement of pressure was to be made. Care is also taken to keep the cell with the finished membrane at the same temperature until it is filled and closed. The solutions, at the time of filling, have always the temperature of the baths in which the cells are to be placed.

The slipping of the manometers in the rubber stoppers, with possible distortion of the latter, has been referred to[1] as a troublesome phenomenon in the earlier work, which, in the more recent measurements, had been largely overcome[2] by improvements in method and manipulation. Still further

[1] THIS JOURNAL, **36**, 23, 50; **37**, 328 and 460.

[2] *Ibid.*, **37**, 460.

Table XXII.—Results for Each Experiment, if Correction Is Made for the Whole Loss in Rotation.

Weight normal concentration.	No. of experiment.	Temperature.	Correction. Atmospheres.	Osmotic pressure. Atmospheres.	Calculated gas pressure. Atmospheres.	Molecular osmotic pressure. Atmospheres.	Molecular gas pressure. Atmospheres.	Ratio of osmotic to gas pressure.
1	2	3	4	5	6	7	8	9
0.1	1	0°.28	0.01	2.40	2.23	23.95	22.28	1.074
"	2	0°.24	0.00	2.40	2.23	24.03	"	1.077
0.2	1	0°.12	0.05	4.66	4.45	23.29	"	1.047
"	2	0°.13	0.03	4.68	4.45	23.39	"	1.051
0.3	1	0°.19	0.05	7.04	6.68	23.45	"	1.054
"	2	0°.25	0.06	7.04	6.68	23.48	"	1.054
0.4	1	0°.13	0.08	9.35	8.91	23.37	"	1.049
"	2	0°.23	0.09	9.33	8.91	23.33	"	1.047
0.5	1	0°.17	0.07	11.69	11.14	23.39	"	1.050
"	2	0°.24	0.12	11.69	11.14	23.38	"	1.049
0.6	1	0°.12	0.22	14.12	13.36	23.53	"	1.057
"	2	0°.08	0.22	14.12	13.36	23.53	"	1.057
0.7	1	0°.08	0.17	16.44	15.59	23.49	"	1.055
"	2	0°.06	0.10	16.42	15.59	23.46	"	1.053
0.8	1	0°.13	0.22	18.86	17.82	23.57	"	1.058
"	2	0°.13	0.17	18.86	17.82	23.58	"	1.058
0.9	1	0°.16	0.35	21.37	20.05	23.74	"	1.066
"	2	0°.15	0.20	21.40	20.05	23.75	"	1.067
1.0	1	0°.17	0.34	23.77	22.28	23.77	"	1.067
"	2	0°.17	0.30	23.72	22.28	23.72	"	1.064

Mean ratio = 1.058

Table XXIII.—Results for Each Concentration, if Correction Is Made for the Whole Loss in Rotation

Weight normal concentration.	Temperature.	Osmotic pressure. Atmospheres.	Calculated gas pressure. Atmospheres.	Molecular osmotic pressure. Atmospheres.	Molecular gas pressure. Atmospheres.	Ratio of osmotic to gas pressure.
1	2	3	4	5	6	7
0.1	0°.26	2.40	2.23	23.99	22.28	1.076
0.2	0°.13	4.67	4.45	23.34	"	1.049
0.3	0°.22	7.04	6.68	23.47	"	1.054
0.4	0°.17	9.34	8.91	23.35	"	1.048
0.5	0°.21	11.69	11.14	23.39	"	1.050
0.6	0°.10	14.12	13.36	23.53	"	1.057
0.7	0°.07	16.43	15.59	23.48	"	1.054
0.8	0°.13	18.86	17.82	23.58	"	1.058
0.9	0°.16	21.39	20.05	23.75	"	1.067
1.0	0°.17	23.75	22.28	23.75	"	1.066

Mean ratio = 1.058

progress has been made in this direction, as will be seen on inspecting column 5 of Table XXI. In the present series the displacement of the manometers was less than ever before, and is wholly negligible as a source of dilution of the cell contents.

Dilution, due to the sucking in of water from the wall[1] while the cell is being closed at the beginning, and opened at the conclusion, of an experiment continues to affect our results, but in a considerably diminished degree, as will be seen by inspecting columns 6, 7 and 8 of Table XXI. The correction for dilution (column 8) is less than on any previous occasion; and, owing to the elimination of the dilution due to manometer displacements, it is of a much less uncertain character than formerly. The loss in the rotation of the solutions while in the cells, which is the measure of the dilution from all causes, has shown a gratifying decrease from the first. In the earliest series[2] of measurements in which the polariscope was used, it amounted to 2.8 per cent; in the second,[3] to 1.49 per cent; and in the third,[4] to 1.47 per cent. In the present series

[1] THIS JOURNAL, **36**, 26, 49; **37**, 327.
[2] *Ibid.*, **36**, 39.
[3] *Ibid.*, **37**, 324.
[4] *Ibid.*, **37**, 425.

Table XXIV.—Results for Each Experiment, if Correction Is Made for Half the Loss in Rotation.

Weight normal concentration.	No. of experiment.	Temperature.	Correction. Atmospheres.	Osmotic pressure. Atmospheres.	Calculated gas pressure. Atmospheres.	Molecular osmotic pressure. Atmospheres.	Molecular gas pressure. Atmospheres.	Ratio of osmotic to gas pressure.	Ratio of Δ to 1.85.
1	2	3	4	5	6	7	8	9	10
0.1	1	0°.28	0.005	2.39	2.23	23.90	22.28	1.071	1.038
"	2	0°.24	0.000	2.40	2.23	24.03	"	1.077	"
0.2	1	0°.12	0.025	4.64	4.45	23.16	"	1.041	"
"	2	0°.13	0.015	4.66	4.45	23.31	"	1.048	"
0.3	1	0°.19	0.025	7.01	6.68	23.38	"	1.050	"
"	2	0°.25	0.030	7.01	6.68	23.38	"	1.049	"
0.4	1	0°.13	0.040	9.31	8.91	23.27	"	1.045	"
"	2	0°.21	0.045	9.29	8.91	23.21	"	1.042	"
0.5	1	0°.17	0.035	11.66	11.14	23.32	"	1.047	"
"	2	0°.24	0.060	11.63	11.14	23.26	"	1.044	"
0.6	1	0°.12	0.110	14.01	13.36	23.34	"	1.048	"
"	2	0°.08	0.110	14.01	13.36	23.34	"	1.048	"
0.7	1	0°.08	0.085	16.36	15.59	23.37	"	1.049	"
"	2	0°.06	0.050	16.37	15.59	23.39	"	1.050	"
0.8	1	0°.13	0.110	18.75	17.82	23.43	"	1.052	"
"	2	0°.13	0.085	18.78	17.82	23.47	"	1.054	"
0.9	1	0°.16	0.175	21.19	20.05	23.54	"	1.057	"
"	2	0°.15	0.100	21.30	20.05	23.66	"	1.062	"
1.0	1	0°.17	0.170	23.60	22.28	23.60	"	1.059	"
"	2	0°.17	0.150	23.57	22.28	23.57	"	1.055	"

Ratio of Δ to 1.84 = 1.044

Mean ratio = 1.052

Table XXV.—Results for Each Concentration, if Correction Is Made for Half the Loss in Rotation.

Weight normal concentration.	Temperature.	Osmotic pressure. Atmospheres.	Calculated gas pressure. Atmospheres.	Molecular osmotic pressure. Atmospheres.	Molecular gas pressure. Atmospheres.	Ratio of osmotic to gas pressure.	Ratio of Δ to 1.85.
1	2	3	4	5	6	7	8
0.1	0°.26	2.40	2.23	23.97	22.28	1.074	1.038
0.2	0°.13	4.65	4.45	23.24	"	1.045	"
0.3	0°.22	7.01	6.68	23.38	"	1.050	"
0.4	0°.17	9.30	8.91	23.24	"	1.044	"
0.5	0°.21	11.65	11.14	23.29	"	1.046	"
0.6	0°.10	14.01	13.36	23.34	"	1.048	"
0.7	0°.07	16.37	15.59	23.38	"	1.050	"
0.8	0°.13	18.77	17.82	23.45	"	1.053	"
0.9	0°.16	21.25	20.05	23.60	"	1.060	"
1.0	0°.17	23.59	22.28	23.59	"	1.057	"

Ratio of Δ to 1.84=1.044 Mean ratio = 1.052

the average loss amounts to only 0.90 per cent of the original rotation. The improvement is due to the elimination of manometer displacement already referred to, to increased rapidity of manipulation, and to the practice, recently introduced,[1] of dipping the cells before closing, and again before opening them, in a solution of sugar, the concentration of which is equivalent to that of the solution within the cell. The suppression of the dilution of the cell contents appears to us the most important of the problems of method which remain to be solved. It is hoped that this can be accomplished by so changing the construction of the cells that they can be more quickly opened or closed, and by diminishing the area of the membrane as compared with the capacity of the cell.

The results, as they would be if correction is made for the whole loss in rotation, are brought together in Tables XXII. and XXIII., and again in Tables XXIV. and XXV., as they would be if correction is made for only one-half the loss in rotation. The reason for believing the results as presented in Tables XXIV. and XXV. the more nearly correct ones has al-

[1] THIS JOURNAL, 37, 464.

ready been given,[1] but it will be restated. The dilution of the solutions which causes nearly all the loss in rotation occurs at two separate periods: First, while the cells are being closed; and second, while they are being opened. The former affects the observed osmotic pressure, and a correction for it is to be applied, if possible; while the latter is without effect upon the measurement and is to be neglected. The observed loss in rotation, however, covers all dilution and it is not practicable to ascertain precisely what proportion of it occurred during the first period, *i. e.*, while the cell was being closed. Formerly, the time required to open a cell was about equal to that consumed in closing it, and for this reason alone it was assumed to be safe to correct for only one-half the observed loss in rotation. That in so doing we did not undercorrect the results appeared probable from the fact that during the closing period the contents of a cell are constantly under considerably increased pressure, while during the opening period they are continuously under diminished pressure, which latter condition necessarily facilitates the entrance of water from the wet wall of the cell. We did not, however, rest with this solution of the problem. A careful record was kept of the time consumed in closing and opening each cell. On comparing these records with the observed losses in rotation, it was clear that more dilution occurs in a given time while a cell is being opened than while it is being closed. Of late we have been able to reduce the time required to open a cell as compared with that consumed in closing it, but not sufficiently, up to the present time, to justify us in correcting for more than one-half the loss of rotation.

It will be seen in Tables XXII., XXIII., XXIV. and XXV that, in the vicinity of 0°, the osmotic pressure of glucose solutions considerably exceeds the calculated gas pressure for the same temperatures. In this respect the conduct of glucose is analogous to that of cane sugar.[2] The divergence from gas pressure is, however, greater and also more irregular in the case of cane sugar than in that of glucose.

[1] THIS JOURNAL, 37, 463.
[2] *Ibid.*, 37, 425.

The ratio of osmotic to gas pressure (Table XXII., column 9; XXIII., column 6; XXIV., column 9; XXV., column 7) appears to be largest in the case of the 0.1 weight-normal solution, to decrease somewhat and then to increase slightly with increasing concentration. A similar but more marked relation was observed in the case of cane sugar.[1] We do not, however, regard this relation as well established for glucose. The variations are not large, and they are such, we believe, as our experimental errors would be likely to produce. It has been stated in former papers that we add a small quantity of potassium ferrocyanide to the sugar solutions (8.46 mg. to 100 grams of water) and a supposed osmotically equivalent quantity (12.48 mg. to 100 grams of solvent) of copper sulphate to the water in which the cell is located during a measurement. Doubt has also been expressed[2] as to the exact osmotic equality of these concentrations of the membrane formers. Recent determinations of the freezing points of potassium ferrocyanide solutions[3] indicate a higher degree of dissociation than has hitherto been ascribed to that substance. Moreover, we have observed that when smaller quantities of the membrane formers are used in determining the osmotic pressure of dilute solutions, slightly lower pressures are obtained, which suggests that the ferrocyanide, in the quantity usually employed, exerts a somewhat greater osmotic pressure than the copper sulphate. Any overpressure on the part of the ferrocyanide, though small absolutely, would affect very decidedly, in the case of the 0.1 normal solution, such relative values as the molecular osmotic pressure, the ratio of osmotic to gas pressure, etc. The same is true of certain possible experimental errors of a constant character. The effect of such errors would diminish rapidly with increasing concentration—sinking to one-half in the case of the 0.2 normal, and becoming insignificant in that of the higher members of the series. We are therefore prepared, in the course of later work, to find for the 0.1 normal solution a smaller ratio of osmotic to gas pressure than that given in the tables, namely, 1.074. It

[1] THIS JOURNAL, **37**, 425.
[2] *Ibid.*, **37**, 466.
[3] *Ibid.*, **34**, 311.

would seem to be an easy matter to determine the osmotic inequality of the membrane formers, but we have found it otherwise. They cannot be omitted, and when we have tried to solve the problem by varying the quantities used, *e. g.*, by reducing them to one-half, the results have not been satisfactorily concordant. A possible explanation of the observed lack of agreement among the results of supposedly equivalent experiments is to be found in the fact that probably varying numbers of the ferrocyanogen ions are used up in repairing the membranes. It is to be remembered that the values in question amount, at most, to only a few—possibly 4 or 5—hundredths of an atmosphere.

The effect of errors of calibration and of reading, on the other hand, increase with the concentration of the solutions, and, on that account, we are also prepared for some slight revision of the osmotic-gas ratios at the other end of the series. We should expect to find about the same degree of concordance among these ratios as is observed in solutions of equal concentration in respect to the molecular depression of the freezing point.[1]

The question which first suggests itself concerns the relation of the excess of osmotic over gas pressure to the difference between the values 1.92 and 1.85, the former number representing the observed molecular depression of the freezing point of weight-normal solutions of glucose, and the latter, the calculated molecular depression of the freezing point of water. For the purpose of such a comparison, column 10 has been added to Table XXIV, and column 8 to Table XXV, under the head of "*Ratio of* Δ *to* 1.85." There is also given the "*Ratio of* Δ *to* 1.84" (the Raoult or experimental value for the molecular depression of the freezing point of water). The value of Δ was found to vary between 1.92 and 1.91 within weight-normal concentrations ranging from 0.1 to 1.0, but it has been assumed to be constant at 1.92.

The ratio of Δ to 1.85 is 1.038, and that of Δ to 1.84 is 1.044; while the mean ratio of observed osmotic to calculated gas pressure is 1.052. Except in the case of the 0.1 normal solu-

[1] THIS JOURNAL, 37, 360.

tion, the variation of the individual ratios from the mean value 1.052 is not large, and we have given our reasons for thinking that later work will establish a somewhat smaller ratio for that concentration.

The various ratios which have been presented are sufficiently in accord to justify the suspicion that, in the case of glucose solutions, the excess of osmotic over gas pressures in the vicinity of 0°, and the difference between the observed and the calculated depressions of the freezing points are to be referred to one and the same cause. Perfect agreement between these ratios could not be expected because of differences of temperature. The osmotic pressures were determined at temperatures ranging from +0°.06 to +0°.28, while the freezing points lie between —0°.192 and —1°.92.

We shall also compare the excessive osmotic pressures which cane sugar solutions were found to exert in the vicinity of 0° with their so-called abnormal freezing points; but, before entering upon that subject, it is necessary to explain a change in our views regarding the amount of *inversion* which takes place in the cell.

In the first series of measurements of the osmotic pressure of cane sugar solutions,[1] it was attempted to determine the inversion which occurred in the closed cells by the method of Fehling.[2] The quantities of invert sugar which were found in this way were small, insufficient, in fact, to justify any corrections for the concentrations 0.1 to 0.5. From 0.5 to 1.0, on the other hand, the results were more definite, and corrections ranging in value from 0.02 to 0.05 atmosphere were applied to the higher concentrations. We stated[3] at the time that we were "inclined to believe that the inversion of the cane sugar in the more concentrated solutions was greater than it was apparently found to be by the method which was employed to determine it," and that when the work was repeated "the polariscope, instead of Fehling's solution" would be "used to measure the inversion which has taken place in the cell."

On remeasuring the osmotic pressure of cane sugar solu-

[1] THIS JOURNAL, 34, 1.
[2] *Ibid.*, 34, 31.
[3] *Ibid*, 34, 92.

tions a year later,[1] with systematic use of the polariscope, it was found that the loss in rotation was in all experiments greater than could have been anticipated from the quantities of invert sugar which had been found in the previous work by the method of Fehling. It was assumed[2] (overhastily, as appeared later) that the greater portion of the loss in rotation was to be ascribed to *inversion*, and accordingly the results (so far as loss in rotation was concerned) were corrected for inversion only, except in those instances in which a definite amount of *dilution* could be ascribed to manometer displacements. If called upon to deal with the same data at the present time, we should give an alternative statement of results, in which one-half the loss in rotation—after deducting that accounted for by manometer displacement—was ascribed to dilution. The results as stated in the original paper are doubtless somewhat too low, because, in most instances, the whole loss in rotation is ascribed to inversion, and no correction is made for dilution. On the other hand, the results as presented in the alternative statement mentioned above would be too high because of the neglect to correct for inversion. The true osmotic pressures of the solutions will, we think, be found to lie somewhere between the two limits, *i. e.*, between the values obtained by ascribing the whole loss in rotation to *inversion* and those obtained by attributing one-half of it to *dilution*. It will be recalled here that the average extent of the debatable ground in the case in question amounts to 2.8 per cent of the observed pressures. The results, as stated in the original paper, are probably too low by about 1.5 per cent.

The fact that the solutions were probably diluted by water entering from the porous walls while the cells were being closed and opened did not escape attention,[3] but the amount of dilution from this cause was underestimated in the earlier work.

When the measurement of the pressure of glucose[4] solutions was taken up, it was found that the average loss in rota-

[1] THIS JOURNAL, **36**, 39.
[2] *Ibid.*, **36**, 41, 48.
[3] *Ibid.*, **36**, 26, 49.
[4] *Ibid.*, **37**, 324.

tion was 1.49 per cent, notwithstanding considerable improvements which had been made in manipulation. It was this observation which convinced us that we had hitherto ascribed too much of the loss in the rotation of cane sugar solutions to *inversion* and too little to the *dilution* resulting from the sucking in of water from the wall while closing and opening the cell. In the case of glucose, *inversion* was excluded, and all loss of rotation must be ascribed to *dilution* resulting from manometer displacements, or from water acquired from the cell wall during the closing and opening periods.

In Series III. of the measurements of the pressures of cane sugar, which are to be used in the comparison which follows, there was no considerable displacement of the manometers, and the average loss in rotation amounted to 1.47 per cent, as against 0.90 per cent for the corresponding glucose series. The difference is not wholly due to inversion of the cane sugar, but is partly accounted for by the fact that only about half of the cells were "dipped" in the former case, while in the latter all of them were subjected to that treatment. Under the circumstances, it is probable that no error is made in assuming that the greater portion of the loss in rotation, which was observed while measuring the pressures of cane sugar solutions in the vicinity of 0°, was due to dilution rather than to inversion. The observation that, when due allowance is made for improved manipulation as the work progresses, the loss of rotation in cane sugar solutions does not greatly exceed that of glucose solutions caused us, in the paper[1] upon the osmotic pressure of cane sugar solutions in the vicinity of 0°, to state the results in three ways, namely, as they would be: (1) If all loss in rotation is ascribed to inversion; (2) if all loss in rotation is ascribed to dilution; and (3) if one-half the loss in rotation is corrected as dilution. We also stated our conviction that the true pressures would be found to lie between the values found by the first and the third methods. At the present time we can add that the results obtained by correcting one-half the loss in rotation as dilution and neglecting inversion are, in our opinion, very nearly accurate.

[1] This Journal, 37, 425.

Table XXVI.—Results for Each Concentration, if Correction Is Made for Half the Loss in Rotation. Cane Sugar. Series III.

Weight normal concentration.	Temperature.	Osmotic pressure. Atmospheres.	Calculated gas pressure. Atmospheres.	Molecular osmotic pressure. Atmospheres.	Molecular gas pressure. Atmospheres.	Molecular depression of the freezing point.	Ratio of Δ to 1.84.	Ratio of Δ to 1.85.	Ratio of osmotic to gas pressure.
1	2	3	4	5	6	7	8	9	10
0.1	0°.24	2.44	2.23	24.40	22.29	1°.95	1.060	1.054	1.094
0.2	0°.26	4.80	4.46	24.00	"	1°.96	1.065	1.059	1.076
0.3	0°.22	7.16	6.69	23.87	"	1°.95	1.060	1.054	1.071
0.4	0°.24	9.40	8.92	23.50	"	1°.96	1.065	1.059	1.054
0.5	0°.19	11.85	11.14	23.70	"	1°.97	1.071	1.065	1.064
0.6	0°.22	14.25	13.37	23.75	"	1°.98	1.076	1.070	1.066
0.7	0°.23	16.81	15.60	24.01	"	1°.99	1.081	1.076	1.078
0.8	0°.23	19.33	17.83	24.16	"	2°.02	1.098	1.092	1.084
0.9	0°.27	22.13	20.06	24.59	"	2°.03	1.103	1.097	1.103
1.0	0°.25	24.78	22.28	24.78	"	2°.07	1.125	1.119	1.112

Having explained the change of view which has been forced upon us regarding the relative importance of inversion and dilution as causes of loss in rotation, we present Table XXVI. to show how the osmotic pressures in the vicinity of 0° and the freezing points of cane sugar solutions are related to one another with respect to the excess of the former over gas pressure, and the deviation of the latter from the calculated value of 1.85 or the experimental value 1.84.

It will be seen that in the case of the 0.1, 0.2 and 0.3 weight-normal concentrations the ratio of osmotic to gas pressure (column 10) differs considerably from that of Δ to 1.85 (column 9), but that the two ratios are in quite close agreement throughout the remainder of the series. We have already given our reasons[1] for thinking that the osmotic-gas ratios for the most dilute solutions will hereafter be diminished, which would bring them more nearly into agreement with the ratios of Δ to 1.85 or 1.84.

Attention is also called to Table XXVII., which brings out clearly the mutual relations of glucose and cane sugar with respect to the osmotic pressures and freezing points of their equivalent solutions.

If we represent by

P, the osmotic pressure of glucose,

P_1, the osmotic pressure of cane sugar,

Δ, the observed molecular depression of the freezing point of glucose,

Δ_1, the observed molecular depression of the freezing point of cane sugar,

R, the ratio of osmotic to gas pressure for glucose,

R_1, the ratio of osmotic to gas pressure for cane sugar,

then proportions, such as the following, should be found to hold approximately:

1. $P : P_1 :: \Delta : \Delta_1$;
2. $R : R_1 :: \Delta : \Delta_1$;
3. $R : R_1 :: \frac{\Delta}{1.85} : \frac{\Delta_1}{1.85}$; etc.

How they do hold for the proportion $P : P_1 :: \Delta : \Delta_1$ (and

[1] THIS JOURNAL, 37, 466.

consequently for all other proper methods of comparison) is shown in Table XXVII. Exact agreement between the calculated and experimental values is not to be expected, owing to differences of temperature, and the divergences between them should increase with the concentration.

Table XXVII.

Weight normal concentration.	P, osmotic pressure of glucose.	P_1, osmotic pressure of cane sugar.	Δ observed molecular depression of the freezing point of glucose.	Δ_1 molecular depression of the freezing point of cane sugar.	
				Calculated.	Observed.
0.1	2.40	2.44	1.92	1.95	1.95
0.2	4.65	4.80	"	1.98	1.96
0.3	7.01	7.16	"	1.96	1.95
0.4	9.30	9.40	"	1.94	1.96
0.5	11.65	11.85	"	1.95	1.97
0.6	14.01	14.25	"	1.95	1.98
0.7	16.37	16.81	"	1.97	1.99
0.8	18.77	19.33	"	1.98	2.02
0.9	21.25	22.13	"	2.00	2.03
1.0	23.59	24.78	"	2.02	2.07

It appears to have been established by the results published in this paper and the preceding one[1] that, in the vicinity of the freezing point of the solvent, both glucose and cane sugar solutions exert osmotic pressures which differ from the calculated gas pressures in about the same degree that the observed depressions of the freezing points of such solutions differ from those which are calculated by means of the value 1.85.

In view of this conclusion, it is now important to measure, in the vicinity of 0°, the osmotic pressures of the solutions of some substance of which the observed molecular depression of the freezing point is approximately 1.85. It is to be anticipated that such solutions, in the vicinity of the freezing point of water, will be found to exhibit osmotic pressures more in accord with the calculated gas pressures than are those of glucose and cane sugar. We shall undertake this as soon as we have succeeded in suppressing dilution in the cell. Until

[1] THIS JOURNAL, 37, 425

that has been accomplished, our work is necessarily limited to substances, the concentration of whose solutions can be readily and accurately determined after their removal from the cell.

While engaged in the development of a method for the measurement of osmotic pressure, we were frequently assured that there was "*no need*" of such a method, that osmotic pressure could be determined by the freezing point method "*much more readily and far more accurately*" than by any method of direct measurement which could possibly be devised. Moreover, it is made apparent, from time to time, in the current literature, that this idea respecting the sufficiency of the freezing point method as a means of determining osmotic pressure continues to prevail in certain quarters. It may, therefore, not be amiss to recall here one of several of the erroneous conclusions regarding the osmotic pressures of glucose and cane sugar solutions to which the established freezing point data have led. One chemist, who apparently was fully convinced of the adequacy of the freezing point method of determining osmotic pressure, predicted that the pressure of a *volume-normal* solution of cane sugar would be found to be "*just about 35 atmospheres.*" The course of reasoning by which the conclusion was reached may be explained as follows: The theoretical value of Δ is 1.85, but the observed value is 2.66. The estimated gas pressure of a gram-molecular weight of cane sugar at $-2°.66$ (with a volume of 1 liter) is about 22.08 atmospheres. The osmotic pressure at $-2°.66$ will therefore be $\frac{2.66}{1.85} \times 22.08$, or 31.75 atmospheres. At 24°, since osmotic and gas pressure have the same (?) temperature coefficient, the osmotic pressure of a volume-normal solution of cane sugar will be $31.75 + 31.75 \times 0.00366 \times 26.66$, or 34.85 atmospheres.

The conclusion is erroneous by more than 3 atmospheres. The *volume-normal* solution (equivalent to the 1.26806 *weight-normal* solution) of cane sugar exerts an osmotic pressure, at 24°, of just about 31.5 atmospheres. The great error in the above estimate lies in the assumption that, having pre-

dicted from freezing point data a certain osmotic pressure at the temperature of freezing, the pressure at higher temperatures can be calculated by the law of Gay-Lussac for gases. We are not to be understood as denying that the law of Gay-Lussac does hold for osmotic pressure. On the contrary, we are inclined to believe that, with certain restrictions, it does hold, and that the pressure anomalies which appear at low temperatures will be found to disappear gradually at higher temperatures, until osmotic and gas pressures are in accord with respect to temperature coefficient. This, however, is a matter of opinion which has no value, except as it is fortified by experimental proof. The only evidence which we can offer at present is the fact that, in the vicinity of 20°, the osmotic pressures of cane sugar and glucose solutions have been found to agree very closely with those calculated for gases, provided we accept the volume of the solvent, and not that of the solution, as the standard for the gases.

It may be affirmed, in concluding, that though the results presented in this paper and in the preceding one show that the osmotic pressures of glucose and cane sugar solutions in the vicinity of 0° could have been calculated from the freezing points with approximate correctness, any prediction, based upon the same data and the law of Gay-Lussac, as to their pressures at higher temperatures would have been wholly futile. This is true even when the calculations are based upon the weight-normal system for osmotic pressure. To illustrate: The osmotic pressure of the weight-normal solution of cane sugar at about 0° (exactly 0°.25) is 24.78 atmospheres. Its pressure at 24° would be estimated ($24.78 + 24.78 \times 0.00366 \times 23.75 = 26.93$) at 26.93 atmospheres. The observed pressure lies between 24.24 and 24.84 atmospheres, according to the method which is adopted for the correction of the loss in rotation in the cell.

JOHNS HOPKINS UNIVERSITY,
March 27, 1907.

PREPARATION OF THE ANILINE DERIVATIVES OF SUCCINIC ACID AND OF PHTHALIC ACID.

By J. Bishop Tingle and Marshall P. Cram.

In the course of some work on the nitration of certain aniline derivatives, which is being carried out by one of us in conjunction with Mr. F. C. Blanck in this laboratory,[1] it was necessary to prepare fairly large quantities of the aniline compounds of succinic and phthalic acids. Some of the methods which we have employed for this purpose differ in certain respects from those described in the literature; in two cases they are entirely new; moreover, they have all proved to be thoroughly satisfactory and adequate for our purpose, consequently it appears to be desirable to place them on record.

Succinanil, $\begin{matrix} CH_2.CO \\ | \\ CH_2.CO \end{matrix}\!\!>\!NC_6H_5$, was prepared essentially according to the method of Menschutkin,[2] but the mixture of acid, 45 grams, and aniline, 40 grams, was placed in a small retort and heated for 3–4 hours, at 140°–150°, in a paraffin-bath. By this means the water was steadily eliminated and there was absolutely none of the "bumping" which was a source of trouble to Menschutkin. As soon as the action is completed, the retort is removed from the bath and quickly heated by a direct flame. A little aniline and water pass over and then the anil. If the distillation is conducted as rapidly as possible there is no danger of the retort's neck becoming closed. The yield is practically quantitative; from 270 grams of the acid we obtained 330 grams of anil, once recrystallized from alcohol.

The conversion of succinanil into succinanilic acid,

$$C_6H_5NHCOCH_2CH_2COOH,$$

was carried out according to the directions of Menschutkin,[3] by heating the anil with milk of lime, in slight excess. Vigorous boiling for 10 or 15 minutes is necessary to bring the cal-

[1] This Journal, **36**, 605 (1906).
[2] Ann. Chem. (Liebig), **162**, 166 (1872).
[3] *Ibid.*, **162**, 178 (1872).

cium salt into solution. The crystals which form on cooling are separated, treated with hydrochloric acid and the precipitated anilic acid is recrystallized once from water. The yield is 129 grams of purified material from 200 grams of anil.

Laurent and Gerhardt discovered SUCCINANILIDE,

$$C_6H_5NHCOCH_2CH_2CONHC_6H_5,$$

as a by-product in the preparation of succinanil.[1] Menschutkin,[2] who repeated their work, found that, contrary to the statement of Laurent and Gerhardt, one recrystallization from alcohol was quite inadequate for the purification of the substance. He accomplished this by the use of alcoholic potassium hydroxide, which readily acts on the anil, but leaves the anilide unchanged. The yield is very poor. Laurent and Gerhardt only isolated a "small quantity," and Menschutkin obtained 22 grams of crude material from 40 grams of acid and 70 grams of aniline. We find that the anilide can be easily prepared by heating succinanilic acid, 50 grams, with aniline, 40 grams, in a reflux apparatus at 180°, during 5 working days. The product was treated twice with excess of cold, dilute hydrochloric acid to remove the unchanged aniline and, after being washed with water, was boiled for about 5 minutes with a clear filtered potassium hydroxide solution, consisting of 12 grams of stick potash in 250 cc. of 95 per cent alcohol, to dissolve any succinanil and succinanilic acid which might be present. Finally, it was recrystallized from alcohol. The yield was 17.1 grams of purified material, *i. e.*, 24.8 per cent of the theoretical quantity. We think that the yield might have been improved by heating the mixture of succinanilic acid and aniline under pressure, but a steel bomb was not available and the use of sealed tubes would have involved a good deal of extra trouble. Some little time after the completion of this part of our work, Arnold Reissert and Arnold More[1] described a method of preparing malonanilide by boiling ethyl malonate with aniline for a short time and then distilling off the alcohol as it is produced. They do not appear

[1] Ann. chim. phys. [3], **24**, 179 (1848); Ann. Chem. (Liebig), **68**, 29 (1848).
[2] *Ibid.*, **162**, 187 (1872).
[3] Ber. d. chem. Ges., **39**, 3300 (1906).

to have tested the behavior of ethyl succinate under these conditions. We are indebted to Mr. H. N. Morse for carrying out an experiment with ethyl succinate and aniline, according to the method of Reissert and More. After boiling these substances for about 30 minutes with a reflux condenser, the condenser was reversed and the material slowly distilled. The heat was applied by means of a bath containing sulphuric acid. The distillate consisted chiefly of aniline, in quantity almost equal to that originally used. The residue contained a relatively large amount of ethyl succinate, together with a small quantity of solid. The results of this experiment indicate, therefore, that the procedure of Reissert and More is not applicable to ethyl succinate and that our method for preparing succinanilide is superior to any which has, hitherto, been described.

Preparation of the Aniline Derivatives of Phthalic Acid.

Of the various methods which have been suggested for the preparation of PHTHALANIL, that of Zincke and Cooksey[1] appeared to us to be the most convenient. It consists in adding the necessary quantity of aniline to a glacial acetic acid solution of phthalic acid, and allowing the mixture to remain for some hours at the ordinary temperature. When we attempted to carry out this experiment we found that the solubility of phthalic acid in glacial acetic acid is so very small, being only about 1.7 grams in 100 grams, at the ordinary temperature, that the preparation of the quantity of material which we needed would have involved a, relatively, very large expenditure of time and acetic acid. Our experiments were, therefore, conducted as follows: Phthalic acid, 200 grams = 1 mol. and glacial acetic acid, 500 grams, were mixed and aniline, 112 grams = 1 mol., was added. After heating this material on a water-bath during 2 working days, water was added and the product filtered. The residue consisted of a mixture which could not be separated by repeated extraction with alcohol. In these circumstances, the portion which had not dissolved in alcohol and the part which deposited on cooling the alcoholic

[1] Ann. Chem. (Liebig), **355**, 375 (1889).

solution were mixed, and boiled for 10 minutes with a solution of 20 grams of dry sodium carbonate in 500 cc. of water. A portion dissolved; the remainder, after being washed and dried, weighed 100 grams and melted at 203°–206°; it was, therefore, practically pure phthalanil, for which Zincke and Cooksey[1] give the melting point 203° and Dobner[2] 205°. The former chemists omit all reference to the yield which they obtained, whereas the latter reports a "theoretical yield" by the distillation of phthalic anhydride and aniline. The yield by our method, as already noted, is 50 per cent of the phthalic acid employed, and if we were repeating our preparation we should omit the treatment with alcohol and boil the precipitate from the diluted acetic acid directly with sodium carbonate. Even with this simplification our method does not appear to be as good as Döbner's, though it is decidedly superior to that of Zincke and Cooksey. There is no indication in the paper of their reason for ignoring Döbner's method, but they state distinctly that "heating should be avoided." Having obtained all the material which we needed we did not consider it necessary to repeat Döbner's work. If there is ground for distrusting it, then our method appears to be the best and most convenient hitherto suggested for the preparation of phthalanil.

At a later stage of our investigation we found that phthalanilic acid could be easily prepared from its constituents without the use of a solvent. Phthalic acid, 10 grams, and aniline, 14.6 grams = about 2.25 mol., were mixed and allowed to remain at the ordinary temperature for 22 minutes. The flask was found to have become hot and steam had condensed in its upper portion; moreover, the mixture had become very stiff. More aniline, 6.7 grams, was now added and the substance heated on a boiling water-bath. After 7 minutes a portion was removed, washed with cold alcohol and recrystallized from more alcohol. At first the solution was pink, but it became yellow as the heating continued. The product melted at about 160°, resolidified and melted again at 190°–195°; it contained a considerable proportion of nitrogen, as shown

[1] *Loc. cit.*

[2] Ann. Chem. (Liebig), **210**, 267 (1881.)

by the sodium test. A portion which had been washed, but not recrystallized, behaved in a similar manner. The heating was continued for 4 hours on the water-bath and another portion withdrawn; after purification in the manner described it gave the same results. A further 5 hours' heating, 9 hours altogether, gave a product which was chiefly phthalanilic acid, but the alcoholic washings, containing, of course, the excess of aniline, after standing for a time at the ordinary temperature, deposited phthalanil. This is certainly the easiest method known to us for making phthalanilic acid and the yield appeared to be very good. We did not investigate the matter further because we had already obtained as much of the acid as we required. We refer later (p. 601) to the readiness with which phthalanil is formed from phthalanilic acid in the presence of an excess of aniline.

PHTHALANILIC ACID was obtained, without difficulty, from phthalanil by the method of Zincke and Cooksey,[1] which consists in treating the phthalanil with alcoholic potassium hydroxide and acidifying the resulting potassium salt. Our product melted at 164°, resolidified and melted again at 204°, showing that at its melting point this acid is changed into phthalanil. The yield was 25.5 grams of acid from 73 grams of phthalanil.

We carried out a considerable number of experiments with aniline and phthalic and phthalanilic acids, respectively, with the object of preparing PHTHALANILIDE, either in the manner employed for obtaining succinanilide (*vide* p. 597), or directly from the constituents. It was quickly evident that the anilide is, relatively, highly unstable and, like the anilic acid, is very readily transformed into the anil. We tried careful regulation of the temperature, with and without the use of aniline in excess. We obtained the phthalanilide in several experiments, but on repeating them it became manifest that this result was dependent on conditions beyond ordinary control and, consequently, we cannot regard the problem as being solved at all to our satisfaction. We give below a brief description of our experiments. In the preparation of phthal-

[1] **Ann. Chem. (Liebig), 255,** 375 (1889).

anil by the method of Zincke and Cooksey,[1] we separated the products of the reaction by means of sodium carbonate. On acidification a white precipitate was formed consisting, presumably, of phthalic and phthalanilic acids (*vide* p. 599). This mixture was added to enough aniline to form a stiff paste and heated on a water-bath for about 2 weeks. A portion of the product, washed twice wth cold dilute hydrochloric acid and then recrystallized from alcohol, melted at 230°, which is 1° below the melting point of phthalanilide. The remainder of the aniline mixture was now heated at 140° for 3 or 4 days, and was then found to consist of phthalanil.

In another experiment, phthalic acid, 9 grams, and aniline, 22 grams, were heated on the water-bath for 2 days. The product was purified by means of hydrochloric acid and alcohol, as described above, and melted at 215°–220°. The melting points of phthalanil and of phthalic acid are 203° and 213°, respectively. Boiling for 6 hours with alcohol, or prolonged heating on the water-bath with an additional quantity of aniline caused no change in the melting point of the product. A further 5 grams of aniline were now added and the mixture heated at 120°–130°, for 1.5 days. The product melted at 201°–205°, showing it to be, essentially, phthalanil.

Phthalanilic acid, 5 grams, and aniline, 12.5 grams, were heated at 120°–310°, for 1.5 days; the product melted at about 201° and further heating of the mixture at 140°–190° produced no decided change in this respect. Additional experiments were made with similar mixtures of phthalanilic acid and aniline, at temperatures ranging from that of the room up to the one given by a boiling water-bath. In some cases the product was recrystallized from alcohol, in others washed with cold alcohol, or with cold hydrochloric acid. The substances obtained consisted either wholly of phthalanil, or of mixtures of this with phthalanilic acid; moreover, we found that boiling the alcoholic washings, containing aniline and phthalanilic acid, always resulted in the formation of phthalanil.

A similar series of experiments was carried out with phthalic acid and aniline, but we failed to obtain any of the anilide.

[1] *Loc. cit.*

We found, however, that phthalanilic acid, as already stated, is easily prepared by simply mixing phthalic acid, 1 mol., with aniline, 2.5 mol., at the ordinary temperature.

We think our results indicate that, although the formation of succinanilic acid and of phthalanilic acid take place in a similar manner, yet in the presence of aniline the further reaction of these substances is quite different, the former yielding succinanilide and the latter phthalanil; moreover, this difference is not by any means simply a question of relative stability at a given temperature, because, as our experiments show, phthalanilic acid is more unstable at the temperature of a boiling water-bath, in the presence of a large excess of aniline, than in its absence. One experiment in support of this has already been given (p. 601) and 2 others may be cited. Phthalic acid, 10 grams, was mixed with aniline, 14.6 grams=about 2.25 mol., and, as it became thick more aniline, 6.7 grams, was added and the mixture heated in an open flask, on the water-bath, for 10 hours. After being washed with cold alcohol the solid residue was found to consist of phthalanilic acid. The alcoholic washings containing the aniline, without any further heating, soon deposited phthalanil. During a further 5 hours' heating the contents of the flask were accidentally allowed to become dry, as the excess of aniline is readily volatile in the steam formed during the reaction. The product was still phthalanilic acid. It was now moistened with aniline, allowed to remain at the ordinary temperature over Sunday, and then heated on the water-bath for a working day (8 hours). This treatment converted it completely into phthalanil.

The second experiment, illustrating the same point, is as follows: Phthalanilic acid, 3 grams, was mixed with enough aniline to form a thick paste and heated on a boiling water-bath for 2 minutes. A portion was removed, washed with cold alcohol and dried. It melted at about 145°, resolidified and then melted at about 200°, showing that it was unchanged phthalanilic acid. The alcoholic washings, after being concentrated, deposited phthalanil. The flask having been off the water-bath for 13 minutes, was now reheated for 2 minutes

and a portion of the product tested. It behaved exactly like the first specimen. The flask having been off the bath for 12 minutes was now again heated for 6 minutes. The product was phthalanil. Eleven minutes' additional heating produced no further change. It may be mentioned that the solubility of phthalanil in alcohol is altogether too slight for it to have been removed from the product of the reaction by washing at the ordinary temperature and that it must, therefore, have been formed in the wash liquors. These experiments show that, whereas 15 hours' heating on the water-bath and one night's standing at the ordinary temperature is not sufficient to convert phthalanilic acid into phthalanil in the absence of excess of aniline, yet in the presence of such an excess the change is complete after 10 minutes' heating and 23 minutes' standing.

The phthalanilide which we required was finally prepared from aniline and phthalyl chloride, according to the method of Rogrow.[1] After recrystallization from alcohol it melted at 232°–233°, the temperature given in the literature being 231°.

The phthalyl chloride was obtained essentially according to the method of Claus and Hoch[2] and of Graebe.[3] Phthalic anhydride, 50 grams = 1 mol., was mixed with powdered phosphorus pentachloride, 70 grams = 1 mol., and heated in a reflux apparatus at 120°–170°, during 8 hours. Inadvertently, the temperature was allowed to rise for a short time to 210°. The phosphorus oxychloride was volatilized under the ordinary pressure and the residue distilled; it boiled at about 47° (130 mm.). After standing for an hour the distillate deposited crystals which were proved to consist of unchanged phthalic anhydride; they were removed by filtration and the liquid chloride gradually added to an alcoholic solution of aniline, in the manner indicated above. The yield of purified chloride was 22.6 grams and about 22 grams of unchanged phthalic anhydride were recovered. The above experimental conditions offer the great advantage of yielding a product which is, apparently, entirely free from chlorine substitution products isomeric

[1] Ber. d. chem. Ges., **30**, 1442 (1897.)
[2] *Ibid.*, **19**, 1187 (1886).
[3] Ann. Chem. (Liebig), **238**, 329 (1887).

with phthalyl chloride, and from phthalyl tetrachloride. These substances were encountered by the chemists mentioned above, and their separation caused a good deal of trouble and loss of material. We attribute our success chiefly to the distillation of the crude material under reduced pressure, and believe that the yield of phthalyl chloride could be improved by the use of a larger proportion of phosphorus pentachloride, without much danger of the formation of isomeric chlorine compounds. The work is being continued by one of us in conjunction with Mr. Lovelace.

JOHNS HOPKINS UNIVERSITY,
December, 1906.

A FORMALDEHYDE COLOR TEST FOR PROTEIDS. I.

BY S. F. ACREE.

[The writer is indebted to the Carnegie Institution of Washington for aid in this work.]

The biuret reaction was considered up to within the last 5 years to be the most reliable of the numerous color tests for the proteids. It was supposed that by this reaction we could differentiate the proteids from the decomposition products, as the former and only the former, with very few exceptions, always gave this color reaction. But concurrently with the synthesis of the large number of polypeptides by Emil Fischer, Theodor Curtius and their co-workers, it has been discovered that a very large number of these polypeptides give the biuret reaction fully as well as the complex proteids. Furthermore, it has recently been found that a number of substances that behave like peptones, and that are much more complicated than even the most complex synthetical polypeptides, do not give the biuret reaction.[1]

Since the reliability of this reaction has been so often questioned, the writer has been led to develop another color test for the proteids, in the hope that it might prove to be a more reliable reaction than the biuret test. The results have proved so satisfactory that a preliminary announcement is now made.

[1] For a general discussion and references see Cohnheim, "Chem. d. Eiweisskörper," 1904, p. 61.

The writer hopes that others who are working with proteid substances or their decomposition products will apply this test and publish their results, so that we can learn just how far this particular color reaction is of value in attempting to decide if the given substance is a complex proteid.

It was found in the course of a study of the Hehner test for formic aldehyde in milk, that the casein and other proteid constituents are the substances that give the color test, and that several other proteids behave similarly;[1] that is, if a very small amount, about 0.01 gram, of casein or lactalbumin is mixed with 0.1 cc. of 1:5000 formic aldehyde solution and to this there is added 0.5 cc. of commercial concentrated sulphuric acid, a violet zone is formed between the sulphuric acid and the solution. The writer has seen statements in the literature that a few proteids give this color test, but so far as he is aware no work has been done to determine if the test is a general one for proteids. Other work on the relation of the concentration of the solutions to the intensity of the color is being done. It can be stated now that a concentrated solution of formic aldehyde must not be used, and that one of the concentration 1:5000 is very satisfactory. We are, furthermore, trying experiments with various other aldehydes, ketones, etc. The formic aldehyde must be allowed to react on the proteid first, and then the concentrated commercial sulphuric acid is added. If the acid is added to the proteid first, and then the formic aldehyde is added, the colored substance is not formed, or at best is formed only very slowly. If a check test with the same amounts of water, instead of the formic aldehyde solution, proteid and acid is made, no color is developed. Since formic aldehyde reacts very readily with proteids,[2] it is probable that the formic aldehyde-proteids react with the acid and give the colored compounds. The fact that when water is added to the mixture the color is not discharged makes it appear probable that the colored compounds are not colored carbinol salts,[3] but salts of bases with

[1] Acree: J. Biol. Chem., **2**, 145.

[2] Blum: Z. physiol. Chem., **22**, 127; Schwartz: *Ibid.*, **31**, 460; Benedicenti: Arch. Anat. physiol., 1897, p. 217.

[3] Acree: Ber. d. chem. Ges., **37**, 626.

chromophore groups. The nature of these colored compounds will be made a subject of investigation.

It is seen at once that this color test is so delicate that it would prove to be very valuable for detecting the presence of small quantities of proteids, provided that only proteids give the test. The reaction has been applied to a large number of substances of varying chemical character. It can be stated, in general, *that the formic aldehyde compound of every proteid tested gave a violet color, whereas, no other classes of substances gave this reaction.* In general, such substances as simple organic acids, sugars, alcohols, esters, amides, phenols, urazoles, semicarbazides, amino acids, polypeptides and cyclic nitrogen compounds do not give the slightest color. In a few cases some violet color was developed, but in the check experiments without the formic aldehyde the same color exactly was shown; this was never the case with the proteids tested, and this fact enables us to distinguish the proteids from the non-proteids, so far as tested. In other words, the formic aldehyde reaction, as far as tested, is much better than the biuret reaction for it enables us to differentiate complex proteids from such compounds as polypeptides, uric acid derivatives and pyrimidines.

One very important phase of the work will next be developed. Will this reaction enable us to distinguish the simpler proteids, such as the albumoses, peptones, etc., from the complex proteids or the very simple derivatives? We shall try to secure a large number of these simpler proteids and carry on this work. The writer will be greatly obliged if workers in these fields will send him samples of about 0.10 gram of any complex or simpler proteids on hand, or will make the tests and report them in the literature. It is very likely, of course, that many substances which must be classed between the proteids and the simpler decomposition products will give this color reaction.

The writer is much indebted to Professors Abel, Osborne, Curtius, Grindley, T. B. Johnson, W. Jones, R. Hunt, M. T. Bogert, A. S. Loevenhart, W. F. Koelker, P. A. Levene, Bardachzi, and others, for substances supplied for this work.

The compounds furnished by each are noted in the column "Source." Other compounds were bought in the market; those furnished by Bender & Hobein are marked "B. & H." in the "Source" column. It will be noted that, in a few instances, the same substance from different sources has been tabulated; this was done to see if the substance made by one method might, because of some impurity, give a color test different from that given by the same compound made by a different method. All samples of the same substance behaved alike.

The following table gives a list of the substances tested. In general, 0.01 gram of the substance was treated with 0.10 cc. of 1:5000 formic aldehyde for 2 or 3 minutes and to this was then added about 0.5 cc. of concentrated commercial sulphuric acid so that there were 2 layers. The proteids gave a violet colored zone between the 2 liquids. Check tests were made in many cases by treating 0.01 gram of substance with 0.10 cc. of water and 0.5 cc. of acid. The proteids never gave any color in the check tests, but a few other substances, noted in the tables below, gave colored compounds. The work will be continued. The writer is much indebted to Dr. R. F. Brunel for aid in this work.

SUPPLEMENTARY NOTE.

Since this article was written the writer has had access to the very interesting communication of Otto Rosenheim.[1] A preliminary announcement of this work was made in an article in the *Journal of Biological Chemistry*, August, 1906, which was presented to the editor on Feb. 26th, or some time before Rosenheim's article left his hands. Furthermore, since the writer has been studying this reaction for more than 2 years, as time and the acquisition of substances would permit, he feels that he has a perfect right to continue the work, and will do so along the lines outlined. Although Rosenheim believes the reaction to be a general one for proteids, he does not give any experimental evidence, as the writer does, to

[1] Bio.-Chem. J., 1, 233.

show that it is characteristic of proteids and not of non-proteids.

Rosenheim's work is very interesting in that he thinks it probable that the tryptophan (indole) group is the basis of the color changes, as is the case with the Adamkiewicz reaction. It should be pointed out, however, that Konto[1] has shown that indole alone gives the test. Perhaps other groups may be concerned, or give the color entirely independently of tryptophan. Only the isolation and thorough study of the colored substance, or substances, can give the evidence needed to clear up the question. A sample of tryptophan kindly furnished by Dr. P. A. Levene gave a reddish-violet color, and a faint green color in the check test. A sample of the same substance, for which I am indebted to Bardachzi, gave a violet color with much more red than the sample prepared by Levene, but the check test gave the same light green color. The tryptophan is inserted in the list of proteids merely for comparison. Although the writer had intended to take up these reactions, he will not interfere with Rosenheim's work, but the writer cannot wholly agree with Rosenheim in regard to the mechanism of the reaction. Rosenheim believes (p. 234) that the reaction may take place in either one of two ways: (1) The formic aldehyde is oxidized first, giving rise to an intermediate oxidation product which reacts with the proteid, or (2) the formic aldehyde may combine with the proteid first, the resulting aldehyde-proteid compound being subsequently oxidized. Rosenheim believes that (1) is a possible explanation because an aqueous suspension of ammonium compound of diformic aldehyde peroxide hydrate was found to give the characteristic color with the proteid and sulphuric acid. The writer believes that all the experimental evidence now at hand excludes (1) and points to (2) as the course of the reaction. In the first place, the writer has never been able to get the color test well if the aldehyde-proteid compound was not formed first; if the proteid is added to the acid first and the formic aldehyde is added afterwards the color appears very slowly; the acid probably polymerizes the formic aldehyde and acts

[1] Z. physiol. Chem., **48**, 185.

upon the proteid so that the formic aldehyde-proteid compound cannot be formed. The reason is not clear. If some such intermediate oxidation product of formic aldehyde is really first formed according to (1), as the test is usually made, and if it then reacts with the proteid in the presence of the acid, it is not apparent why such a series of reactions should not take place readily when the acid is added to the proteid before the formic aldehyde is added. It might be objected by Rosenheim that the oxidizing agent present in the acid is used up by the proteid when the proteid is first added to the acid, and that there is no oxidizing agent present then to act upon the formic aldehyde when it is added. This objection is met by the fact that when a mixture of the commercial acid and globulin from squash-seed are treated with the formic aldehyde the color appears very slowly. But when this very same proteid-sulphuric acid solution is added to some of the proteid-formic aldehyde compound the colored substance is formed at once. The formation of the color test by the use of ammonium compound of diformic aldehyde peroxide hydrate is just what we should expect from (2). The compound is probably hydrolyzed to some extent in water[1] into ammonia, hydrogen peroxide and formic aldehyde; the formic aldehyde then reacts with the proteid, and, when the sulphuric acid is added, the necessary constituents, the formic aldehyde-proteid and the hydrogen peroxide, are present to give the color test. It seems then that all the evidence is in favor of explanation (2), the one pointed out by the writer in this article.

Rosenheim states that the gelatin used by him gave no color test. The commercial gelatin used in this laboratory gave the color test slowly, but the writer cannot vouch for the quality of this material. Furthermore, since the samples of gelatoses furnished by Levene also gave faint color tests, it seems probable that there is present some constituent in gelatin which really gives the color test. This may be a very small trace of tryptophan or some other constituent. It is well known that gelatin certainly does not contain very much tryptophan.

[1] Baeyer and Villiger: Ber. d. chem. Ges., 33, 2479. Nef: Ann. Chem. (Liebig), 298, 293.

Experimental Part.

PROTEIDS.

	Substance.	Color.	Check test.	Source.
1	Legumin—horse bean	Violet at once	No color	Osborne
2	Conglutin—yellow lupine	Violet slowly	"	"
3	Ovalbumin (very pure) hen's egg	Violet at once	"	"
4	Vignin—cow pea	Violet slowly	"	"
5	Globulin—cotton seed	Violet quickly	"	"
6	Hardein—barley	Violet at once	"	"
7	Amandin—almonds	" " "	"	"
8	Gliadin—rye	" " "	"	"
9	Novitellin—hen's egg	" " "	"	"
10	Globulin—castor bean	" " "	"	"
11	Inglansen—English walnut	" " "	"	"
12	Glycinin—soy bean	Violet quickly	"	"
13	Excelsin—brazil nut	Violet at once		
14	Globulin—squash seed	Deep violet at once	"	"
15	Edestin—hemp seed	Violet at once	"	"
16	Gliadin—wheat	" " "	"	"
17	Glutenin	" " "	"	"
18	Phaseolin—kidney bean	" " "	"	"
19	Protein—flour	" " "	"	Acree
20	Casein	" " "	"	Casein Co. of America
21	Nucleo-casein	" " "	"	Casein Co. of America

PROTEIDS.—*Continued.*

	Substance.	Color.	Check test.	Source.
22	Milcora from skim milk	Violet at once	No color	Casein Co. of America
23	Albumose	" " "	"	Grindley
24	Coagulum (60°) from water extract of beef	Fine violet at once	"	"
25	Lima bean	Violet at once	"	Acree
26	Saliva	Violet slowly	"	"
27	Keratin	Violet at once	"	Abel
28	Ossein	Violet slowly	"	"
29	Casein—commercial	Violet at once	"	
30	Paracasein	" " "	"	Loevenhart
31	Gelatine—commercial	Violet slowly	"	
32	Beef	Violet at once	"	
33	Milk	" " "	"	
34	White of hen's egg (fresh)	" " "	"	
35	Fish albumin—commercial	" " "	"	
36	Pepsin—commercial	Blue-violet at once	"	
37	Prototryptogelatose	Faint violet-red	Reddish	Levene
38	Deuterotryptogelatose	" " "	"	"
39	I peptone	Red-violet	"	"
40	Mannonucleic acid	Charred	Charred	"
41	Tryptophan	Red-violet	Faint green	"
42	Tryptophan	Red-violet, with more red than with No. 41	" "	Bardachzi

NON-PROTEID SUBSTANCES.

Amino Acids and Polypeptides.

	Substance.	Color.	Check test.	Source.
1	Glycocoll	No color	———	Koelker
2	Leucine nitrate	"	No color	"
3	Asparaginic acid	"	"	"
4	Hippurylalanine	"	"	"
5	Hippurylasparaginic acid	"	"	"
6	Hippurylalanylalanine	"	"	"
7	Hippurylisoserine	"	"	"
8	Tryosine	"	"	"
9	Leucylisoserine	"	"	"
10	Leucylisoserine (B)	"	"	"
11	α-Bromisocapronylisoserine	"	"	"
12	Alanine	"	"	"
13	Benzoylpentaglycylglycine	"	"	"
14	Asparagine	"	"	B. & H.
15	Glycocoll	"	"	"
16	Leucine	Brown	Brown	"
17	Alanine	No color	———	"
18	Taurine	"	———	"
19	Sarcosine	"	———	"
20	Sarcosine	"	———	Kahlbaum
21	Aspartic acid	"	No color	Levene
22	Glutaminic acid	"	"	"
23	Oxyprolein	Light yellow	Light yellow	"
24	α-Prolein	No color	No color	"

NON-PROTEID SUBSTANCES.—*Continued.*

Amides, Ureas, Semicarbazides, Hydrazines.

	Substance.	Color.	Check test.	Source.
25	Triphenylguanidine	No color	No color	Acree
26	1-Phenylthiosemicarbazide	Pink	Deep green	"
27	Semicarbazide hydrochloride	No color	No color	"
28	Phenylsemicarbazide	Deep red	Deep red	"
29	Formamide	No color	No color	B. & H.
30	Acetamide	"	"	"
31	Asparagine	"	"	"
32	Succinimide	"	"	"
33	Succinamide	"	"	"
34	Oxamide	"	"	"
35	Cyanamide	"	"	"
36	Urethane	"	"	"
37	Biuret	"	"	"
38	Thiourea	"	———	"
39	Urea	"	———	"
40	Phenylurea	"	———	"
41	Amidoguanidine nitrate	Violet	Violet	"
42	Phenylurethane	No color	———	"
43	Thiocarbanilide	"	———	"
44	Benzylidinephenylhydrazine	"	———	"
45	Phenacetin	"	———	"
46	*p*-Aminoazobenzene	Red color	Red color	"
47	Acetanilide	No color	———	"

NON-PROTEID SUBSTANCES.—*Continued.*

Amides, Ureas, Semicarbazides, Hydrazines.—Continued.

	Substance.	Color.	Check test.	Source.
48	Amygdalin	Color changing from bright purple at first to a pink	Color changing from bright purple at first to a pink	B. & H.
49	Benzamide	No color	———	"
50	Diazoaminobenzene	Dark brown	Dark brown	"
51	*m*-Aminophenol	" "	" "	"
52	Saccharin	No color	———	"
	Saccharin	"	———	Remsen
53	Carbazole	Light green	Light green	B. & H.
54	Triethylamine	No color	———	"
55	Methylacetanilide	"	———	"
56	Methylamine hydrochloride	"	———	"
57	Cyanacetic acid	"	———	"
58	Xylenesulphonamide	"	———	"

Cyclic Nitrogen Compounds.

	Substance.	Color.	Check test.	Source.
59	1-Phenyl-4-methylurazole	No color	No color	Acree
60	1-Phenyl-3-thio-4-methyl-urazole	"	"	"
61	1-Phenylurazole	"	"	"
62	Xanthine nitrate	"	"	W. Jones
63	Alloxan	"	"	Kahlbaum

Cyclic Nitrogen Compounds.—Continued.

	Substance.	Color.	Check test.	Source.
64	Chitin	No color	No color	Abel
65	Guanine hydrochloride	"	"	W. Jones
66	Uracil	"	"	Johnson
67	Cytosine	"	"	"
68	Thymine	Red color	"	"
69	5-Amino-4-oxyquinazoline	Pink color	Pink color	Bogert
70	2-Methyl-4-oxyquinazoline	No color	No color	"
71	Uric acid	"	"	B. & H.
72	Barbituric acid	"	"	"
73	Alloxantine	"	"	"
74	Theobromine	"	———	"
75	Caffeine	"	———	"
76	Cyanuric acid	"	———	"
77	Murexid	Violet	Violet	"
78	Creatine	No color	———	"
79	Cyamelide	"	———	"
80	Paracyanogen	"	———	"
81	Alloxantine	"	———	"
82	Peptone	"	———	Grindley and Trowbridge
83	Antipyrin	"	———	Kahlbaum
84	Carbazole	Light green	Light green	"
85	Isatin	Dark brown	Dark brown	"
86	Brucine sulphate	No color	———	B. & H.
87	Strychnine	"	———	"

NON-PROTEID SUBSTANCES.—*Continued.*

Cyclic Nitrogen Compounds.—Continued.

	Substance.	Color.	Check test.	Source.
88	Cocaine	No color	———	B. & H.
89	Takadiastase	Brown	———	"
90	Piperine	Dark brown	Dark brown	"
91	Opium	Charred	Charred	"
92	Morphine sulphate	Light purple	Light purple	"
93	Codeine	" "	" "	"
94	Haemoglobin	No color	———	"
95	Haematin	"	———	"
96	Quinine sulphate	"	———	"
97	Quinidine	"	———	"
98	Ethyl dihydrocollidinedicarboxylate	"	———	"
99	Haematein	Dark red, with charring	Dark red, with charring	"
100	Pyridine	Light purple	Light purple	"
101	Lutidine	" "	" "	"
102	Diastase	Brown	Brown	"
103	Nicotine	"	———	"
104	Quinoline	No color	———	"
105	Quinaldine	"	———	"

Sugars and Esters.

	Substance.	Color.	Check test.	Source.
106	Glucose	No color	No color	B. & H.
107	Cane sugar	"	"	"
108	Lactose	"	"	"

NON-PROTEID SUBSTANCES.—*Continued.*

Sugars and Esters.—Continued.

	Substance.	Color.	Check test.	Source.
109	Butter fat	No color	No color	B. & H.
110	Lard	"	"	"
111	Galactose	"	———	"
112	Mannite	"	———	"
113	Dextrin	Dark brown	Dark brown	"
114	Glucovanillin	Charred	Charred	"
115	Creosote oleate	Light brown	Light brown	"
116	Starch	No color	No color	"
117	Lanolin	Brown-red	Brown-red	"
118	Salicin	Purple	Purple	"
119	Coniferin	"	"	"
	Saccharin (*vide* 4)			

Acids and Phenols.

	Substance.	Color.	Check test.	Source.
120	Glycocholic acid	Dark green, changing to purple	Dark green, changing to purple	B. & H.
121	Thymol	Light red	Light red	"
122	Gallic acid	No color	———	"
123	Tannic acid	"	———	"
124	Alizarin	Dark red	Dark red	"
125	Margaric acid	No color	———	"
126	Sebacic acid	"	———	"
127	Hydroquinol	Purple	Purple	"
128	Malic acid	No color	———	"

NON-PROTEID SUBSTANCES.—*Continued.*

Miscellaneous.

	Substance.	Color.	Check test.	Source.
129	Potassium xanthogenate	No color	———	B. & H.
130	Stilbene	"	———	"
131	Phenanthrene	"	———	"
132	Apolysin	"	———	"
133	Solveol	"	———	"
134	Hexachlorethane	"	———	"
135	*m*-Chlornitrobenzene	Purple	Purple	"
136	Ionone	Dark brown	Dark brown	"

It was pointed out in the preliminary notice that other aldehydes had been worked with and that vanillin gives the violet color with proteids very nicely.

The writer will continue the work outlined in this article, but will try not to interfere with Rosenheim's work.

JOHNS HOPKINS UNIVERSITY,
July 1, 1906.

THE DETERMINATION OF TRANSITION TEMPERATURES.

BY DAVID W. HORN.

The object of this paper is to describe a simple method of determining transition temperatures in systems of the second order, consisting of 2 solid phases and a vapor phase. The method is applicable to *dissociation* in systems where 1 of the 2 components has a negligible vapor pressure, while the other component, under the same conditions, constitutes the vapor phase. The method, slightly modified, can be used at different pressures, and in many cases can supply the information heretofore obtained by the far more laborious measurements of vapor pressures.

The time required for a determination ranges from 45 to 90 minutes; it may be reduced to a fraction of that time by using less of the dissociating solid. The amount of substance necessary is very small indeed. The apparatus used in the 4 determinations given in this paper consisted of a thermometer, a small clock with a second hand, and a test tube, supplemented, in some cases, by a filter pump and a water-bath.

The test tube had an internal diameter of about 1.8 cm. and a length of 12 cm. It was closed by a rubber stopper with 2 perforations. Through one of them a thermometer was passed so that its bulb was in the lower end of the test tube when the stopper was in place. In the bottom of the test tube and about the bulb of the thermometer was placed the solid whose temperature of dissociation was to be determined. Through the second perforation in the stopper a delivery tube passed. This delivery tube was bent in such a way that its outer end could be placed beneath a surface of mercury while the test tube and thermometer occupied an almost vertical

position. This arrangement was used when ammonia was the vapor evolved in the dissociation. When water was evolved, the delivery tube was attached to a filter pump. The apparatus can readily be modified to fit other cases. When the delivery tube is lengthened and graduated, pressures considerably above 1 atmosphere can be obtained by inserting the delivery tube in a somewhat wider tube of suitable length containing mercury. Other modifications readily suggest themselves.

I first used the method to locate the temperatures at which higher and unstable cuprammonium compounds decompose into ammonia and simpler and more stable cuprammonium compounds. Borax was then examined as an instance of a dissociating hydrated salt. Sodium bicarbonate was taken to illustrate dissociation when the vapor phase contains more than 1 molecular species. Finally, as a check upon the method, the transition-temperature of the compound $AgCl.3NH_3$ was determined. This substance was selected because the transition temperature can also be obtained by plotting the values for the tensions of ammonia over this compound at different temperatures obtained by Isambert[1] and by Horstmann.[2] A second reason for selecting this substance was that the transition takes place near 20°, the room temperature, where errors due to the exposed stem of the thermometer and other errors affecting its reading are less significant.

The data are given in the tables that follow. The curves plotted from these tables have the same general form as inverted "cooling curves." The horizontal portions represent the transition temperatures, just as the horizontal portions of cooling curves represent freezing points. The methods of obtaining the data and of using it are so simple that they require no discussion beyond that found in the necessary explanations accompanying each of the following experiments.

EXPERIMENT I.

Cuprammonium Nitrate.

The solid examined was a deep blue, crystalline substance

[1] Ann. Ecol. Norm., **5**, 129 (1868).

[2] Ber. d. chem. Ges., **9**, 756 (1876).

obtained when the solvent, liquid ammonia, had evaporated from a solution made by dissolving the compound,

$$Cu(NO_3)_2.4NH_3.$$

As the substance warms to room temperature its color changes from blue to lilac, and ammonia is evolved. The dissociation takes place as follows:

$$Cu(NO_3)_2.5NH_3 \rightleftharpoons Cu(NO_3)_2.4NH_3 + NH_3.$$

The blue nitrate will be discussed in detail along with some other new cuprammonium salts in a separate paper

The air, at about 20°, served as the constant temperature bath. The thermometer used had a scale length of 21.6 cm., and was graduated from —14° to +32°, into tenths. It was read every minute. The time was read from the second hand of a small clock. The readings were continued for 1¼ hours.

The transition temperature was registered by the thermometer between 15°.29 and 15°.31. The reading of the thermometer was practically constant for more than 15 minutes.

EXPERIMENT II.

Borax.

The solid examined was taken directly from the stock bottle in the laboratory, finely ground in a porcelain mortar, and introduced into the test tube in sufficient quantity to cover the bulb of the thermometer. The dissociation takes place as follows:

$$Na_2B_4O_7.10H_2O \rightleftharpoons 5H_2O + Na_2B_4O_7.5H_2O.$$

A water-bath stirred by hand was used. Its temperature was maintained between 69° and 69°.6 The thermometer employed had a scale length of 38 cm. and was graduated from —3° to +60° into tenths. It was read every half minute for about ¾ hour. The delivery tube was connected with an efficient filter pump, which was kept in constant action. This was done because borax, like most other salts

Table I.—Cuprammonium Nitrate.

Time. Minutes.	Temperatures.	Time. Minutes.	Temperatures.	Time. Minutes.	Temperatures.	Time. Minutes.	Temperatures.
0	7°.3	24	16°.39	48	15°.32	73	16°.51
1	8°.5	25	16°.31	49	15°.32	74½	16.°65
2	9°.7	26	16°.27	50	15°.32		
3	10°.9	27	16°.21	51	15°.30		
4	11°.9	28	16°.19	52	15°.30		
5	12°.8	29	16°.10	53	15°.30		
6	13°.57	30	16°.01	54	15°.30		
7	14°.25	31	15°.96	55	15°.30		
8	14°.90	32	15°.89	56	15°.29		
9	15°.48	33	15°.83	57	15°.29		
10	16°.00	34	15°.77	58	15°.30		
11	16°.40	35	15°.72	59	15°.30		
12	16°.80	36	15°.69	60	15°.30		
13	17°.03	37	15°.62	61	15°.30		
14	17°.20	38	15°.52	62	15°.30		
15	17°.28	39	15°.50	63	15°.33		
16	17°.29	40	15°.49	64	15°.40		
17	17°.19	41	15°.43	65	15°.50		
18	17°.04	42	15°.41	66	15°.60		
19	16°.90	43	15°.40	67	15°.67		
20	16°.78	44	15°.37	68	15°.82		
21	16°.63	45	15°.33	69	15°.99		
22	16°.53	46	15°.30	70	16°.13		
23	16°.48	47	15°.30	71	16°.30		

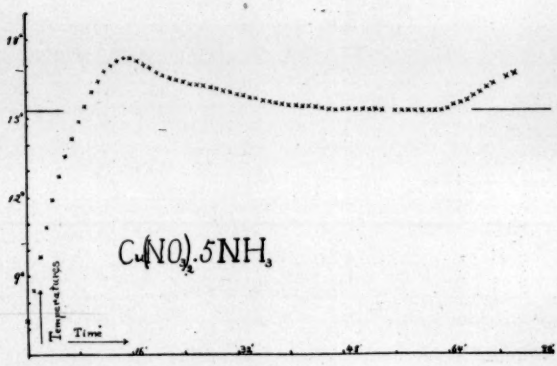


Fig. I.

with water of crystallization, does not exhibit a dissociation pressure equal to 1 atmosphere while the temperature is below 100°. No condensation of the water vapor evolved occurred within the apparatus. When the pump is stopped at the close of the experiment the dissociation is immediately slowed up, and the temperature once more rises very suddenly. The transition temperature registered by the thermometer was 47°.42 to 47°.47 and was maintained practically constant during 7 minutes.

Table II.—Borax.

Time. Minutes.	Temperature.	Time. Minutes.	Temperature.	Time. Minutes.	Temperature.	Time. Minutes.	Temperature.
		11½	47°.86	23½	47°.46	35½	48°.71
0	42°.9	12	47°.82	24	47°.49	36	48°.80
½	44°.3	12½	47°.75	24½	47°.50	36½	48°.87
1	45°.23	13	47°.70	25	47°.50	37	48°.95
1½	46°.2	13½	47°.67	25½	47°.55	37½	49°.02
2	46°.82	14	47°.60	26	47°.60	38	49°.12
2½	47°.30	14½	47°.60	26½	47°.63	38½	49°.18
3	47°.66	15	47°.58	27	47°.69	39	49°.27
3½	47°.92	15½	47°.54	27½	47°.75	39½	49°.37
4	48°.11	16	47°.51	28	47°.80	40	49°.42
4½	48°.25	16½	47°.50	28½	47°.85	41	49°.57
5	48°.30	17	47°.50	29	47°.90	42	49°.68
5½	48°.31	17½	47°.47	29½	47°.99		
6	48°.35	18	47°.47	30	48°.07		
6½	48°.35	18½	47°.46	30½	48°.11		
7	48°.35	19	47°.46	31	48°.16		
7½	48°.35	19½	47°.42	31½	48°.22		
8	48°.25	20	47°.42	32	48°.29		
8½	48°.20	20½	47°.42	32½	48°.35		
9	48°.17	21	47°.46	33	48°.40		
9½	48°.11	21½	47°.47	33½	48°.45		
10	48°.07	22	47°.47	34	48°.51		
10½	48°.00	22½	47°.45	34½	48°.59		
11	47°.94	23	47°.45	35	48°.64		

EXPERIMENT III.

Sodium Bicarbonate.

The solid examined was taken from the laboratory stock. It was not further pulverized. The dissociation takes place as follows:

$$2NaHCO_3 \rightleftharpoons Na_2CO_3 + H_2O + CO_2.$$

A bath of boiling water was used. The thermometer had a scale length of 30.5 cm. and was graduated from 46° to

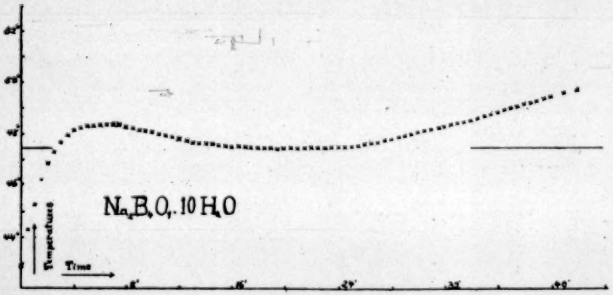


Fig. II.

106°, in tenths. It was read every half minute for about 45 minutes. The filter pump was used continuously as in Experiment II.

The transition temperature registered was 90°.80 to 90°.88. The temperatures remained within these limits about 12 minutes.

EXPERIMENT IV.

Ammonia Silver Chloride.

The solid examined was made from precipitated silver chloride, the precipitate being prepared by pouring hot dilute potassium chloride solution very slowly into a slight excess of hot dilute silver nitrate solution. The precipitate was repeatedly washed with hot water by violently shaking it in a flask with the water in such a way as to break up the clots. The precipitate was collected and placed in a press between pads of filter paper. When as much water had been removed as possible by this method, the precipitate was finely ground and placed, for 24 hours, in a desiccator over sulphuric acid. Before it was used it was heated on

Table III.—Sodium Bicarbonate.

Time minutes.	Temperature.	Time minutes.	Temperature.	Time minutes.	Temperature.	Time minutes.	Temperature.
0	82°.7	8½	93°.00	21	90°.89	33	90°.90
¼	83°.5	9	92°.91	21½	90°.88	33½	90°.90
½	84°.2	9½	92°.80	22	90°.87	34	90°.91
¾	84°.9	10	92°.70	22½	90°.85	34½	90°.92
1	85°.6	10½	92°.55	23	90°.83	35	90°.97
1¼	86°.2	11	92°.41	23½	90°.81	35½	90°.99
1½	86°.9	11½	92°.27	24	90°.80	36	91°.01
1¾	87°.6	12	92°.15	24½	90°.81	36½	91°.01
2	88°.2	12½	92°.02	25	90°.81	37	91°.02
2¼	88°.7	13	91°.90	25½	90°.81	37½	91°.02
2½	89°.3	13½	91°.80	26	90°.81	38	91°.03
2¾	89°.8	14	91°.70	26½	90°.81	38½	91°.05
3	90°.2	14½	91°.59	27	90°.81	39	91°.09
3¼	90°.6	15	91°.50	27½	90°.83	39½	91°.10
3½	90°.95	15½	91°.40	28	90°.84	40	91°.11
3¾	91°.30	16	91°.33	28½	90°.86	40½	91°.12
4	91°.60	16½	91°.28	29	90°.86	41	91°.13
4½	92°.05	17	91°.21	29½	90°.86	42	91°.13
5	92°.48	17½	91°.14	30	90°.86	43	91°.19
5½	92°.73	18	91°.10	30½	90°.86	44	91°.20
6	92°.91	18½	91°.05	31	90°.86	45	91°.28
6½	93°.04	19	91°.00	31½	90°.88	46	91°.38
7	93°.10	19½	90°.96	32	90°.88	47	91°.48
7½	93°.10	20	90°.93	32½	90°.89	48	91°.56
8	93°.09	20½	90°.90				

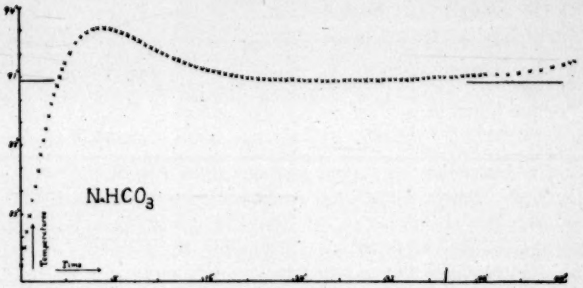


Fig. III.

glass 4 hours at 100°. All of these operations were carried out in the dark. When light was necessary, an electric incandescent lamp, encased in 2 thicknesses of heavy paper was used.

Enough of the dry chloride to cover the bulb of the thermometer was introduced into the test tube, which was protected from light by a movable black paper jacket. Liquid ammonia was drawn upon the chloride until it was completely submerged. After the liquid ammonia had boiled off, the test tube was introduced into a water thermostat at 24°.5. The readings were made every ½ minute, but only some of the readings are given in the table, as the rest were unnecessary for plotting the curve. The thermometer used was the same as in Experiment II.

The transition temperature registered was 19°.39, and not the slightest deviation in the reading of the thermometer could be observed for over 0.5 hour.

After the experiments had been completed the thermometers were corrected. Each thermometer was compared with a standard thermometer when both were immersed in a water-bath at a temperature identical with the transition temperature which the uncorrected thermometer had been used to measure. The standard thermometer was graduated into fifths and had been corrected to 0°.1 degree in September, 1906, by the Physikalisch-Technische Reichsanstalt (PTR 27863). In the following table the corrected transition temperatures are given:

Cuprammonium nitrate	15°.30–15°.32	at	approx.	76	cm. pres.
Borax	47°.9 –48°.0	"	"	2	" "
Sodium bicarbonate	90°.4 –90°.48	"	"	2	" "
Ammoniosilver chloride	19°.4	"	"	76	" "

The last value, as stated, was determined as a test of the method. From Isambert's curve of vapor pressures this temperature should be 19°.9; from Horstmann's, 19°.05; the average of the two is 19°.47. Therefore, the reliability of the method proposed in this paper is certainly within the limits of error in the older vapor pressure method.

Table IV.—Ammonia Silver Chloride.

Time minutes.	Temperature.	Time minutes.	Temperature.	Time minutes.	Temperature.	Time minutes.	Temperature.
0	6°.9	10½	20°.35	24	19°.59	68	19°.39
½	9°.1	11	20°.35	25	19°.55	70	19°.41
1	11°.1	11½	20°.32	26	19°.53	72½	19°.43
1½	12°.7	12	20°.30	27	19°.51	74½	19°.45
2	14°.0	12½	20°.28	28	19°.50	77	19°.49
2½	15°.2	13	20°.22	29	19°.50	79½	19°.51
3	16°.2	13½	20°.19	30	19°.50	82	19°.51
3½	17°.0	14	20°.15	31	19°.49	85½	19°.53
4	17°.65	14½	21°.10	32	19°.45	88½	19°.58
4½	18°.20	15	21°.07	33	19°.44	91½	19°.60
5	18°.70	15½	20°.01	34	19°.42	93½	19°.62
5½	19°.10	16	19°.99	35	19°.41	96	19°.66
6	19°.40	16½	19°.92	36	19°.40	98	19°.71
6½	19°.65	17	19°.89	37	19°.40	102½	19°.75
7	19°.86	17½	19°.86	38	19°.39	104	19°.79
7½	20°.02	18	19°.83	43	19°.39	107	19°.81
8	20°.14	19	19°.78	48	19°.39	116	19°.99
8½	20°.21	20	19°.71	53	19°.39	132	20°.28
9	20°.30	21	19°.69	58	19°.39	142	20°.59
9½	20°.32	22	19°.63	63	19°.39	158	20°.74
10	20°.35	23	19°.60				

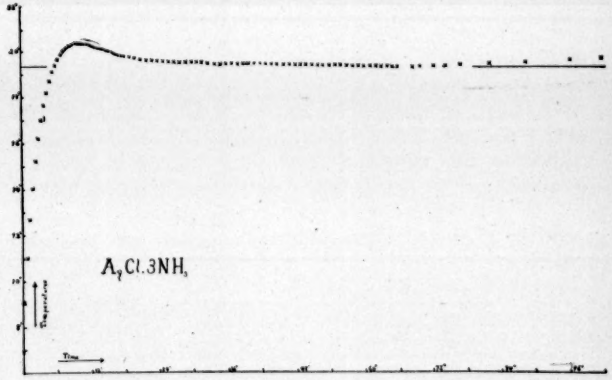


Fig. IV.

The transition temperatures of other solids that absorb heat when they dissociate are under investigation. The method is readily applicable to hydrated salts, ammonia compounds, addition products where the addenda are hydrochloric acid, hydrogen peroxide, hydrogen sulphide, alcohol, ether, benzene, organic bases, etc., as well as to the dissociable compounds like nitrates, carbonates and similar substances. It is applicable to systems of higher orders, such as

$$PbO + NH_4Cl \rightleftarrows Pb(OH)Cl + NH_3.$$

Contributions from the Sheffield Laboratory of Yale University.

CXLIV.—RESEARCHES ON PYRIMIDINES: SOME CONDENSATION PRODUCTS OF A SUBSTITUTED PSEUDOTHIOUREA: SYNTHESIS OF 1-METHYLURACIL.

By Treat B. Johnson and F. W. Heyl.

(TWENTIETH PAPER.)

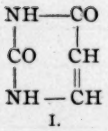
Substituted ureas apparently do not condense with β-ketone esters to form pyrimidines. While urea reacted with ethyl acetoacetate to form 4-methyluracil, II., Behrend[1] obtained no condensation products corresponding to methyluracil when phenylurea, diphenylurea and dimethylurea were treated with this ketone ester.

The alkyl derivatives of 4-methyluracil, II., in which the alkyl groups are linked to nitrogen, have all been prepared by heating this pyrimidine with alkyl halides[2] in presence of alkalis, or by condensing β-alkyluraminocrotonic esters, III., to pyrimidines, by treatment with alkali.[3] The corresponding alkyl derivatives of uracil, I., have not been described.

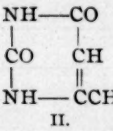
[1] Ann. Chem. (Liebig), **229**, 15; **233**, 1.

[2] Behrend: Ann. Chem. (Liebig), **229**, 23; **231**, 256; **253**, 67. Hagen: *Ibid.*, **244**, 2. Hoffman: *Ibid.*, **253**, 73. Behrend and Dietrich: *Ibid.*, **309**, 260. Behrend and Meyer: Ber. d. chem. Ges., **33**, 624.

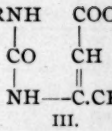
[3] Behrend and Meyer: Ber. d. chem. Ges., **33**, 621. Behrend and Buchholz: Ann. Chem. (Liebig), **314**, 209. Behrend and Thurm: *Ibid.*, **323**, 160. Behrend and Hesse: *Ibid.*, **329**, 341.



I.



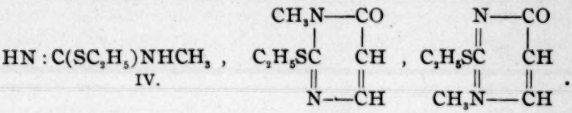
II.



III.

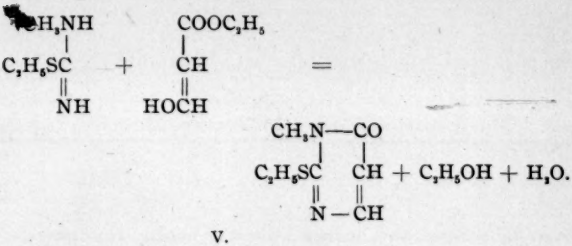
It has been shown in papers from this laboratory[1] that elementary pseudothioureas condense more readily with aldehyde and ketone esters than the normal oxygen ureas. In this paper we describe the behavior of an aliphatic, monosubstituted pseudothiourea towards some ketone esters. We find that they condense to give substituted mercaptopyrimidines, which are easily converted to uracil derivatives by digesting with hydrochloric acid.

Theoretically, 2 isomeric mercaptopyrimidines—1-methyl-2-ethylmercapto-6-oxypyrimidine, V., or 3-methyl-2-ethylmercapto-6-oxypyrimidine, VI., might be formed by condensing ethyl formylacetate with methyl pseudoethylthiourea, IV. We find that they condense to give 1-methyl-2-



IV. V. VI.

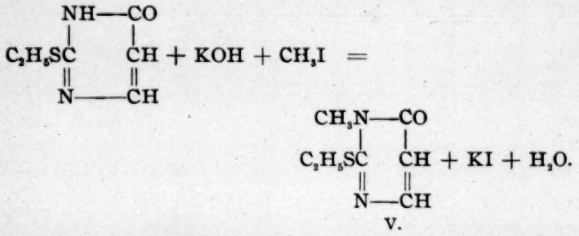
ethylmercapto-6-oxypyrimidine, V. We obtained no evidence of the formation of the isomeric derivative, VI.:



V.

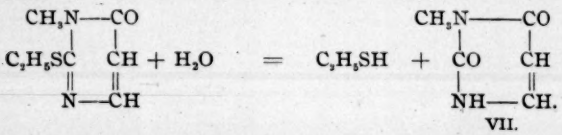
[1] Wheeler and Merriam: THIS JOURNAL, **29**, 478 (1903). Wheeler and Johnson: *Ibid.*, **31**, 591 (1904). Wheeler and Bristol: *Ibid.*, **33**, 437 (1905).

The same mercaptopyrimidine, V., was also obtained when 2-ethylmercapto-6-oxypyrimidine[1] was warmed in alcohol with molecular proportions of potassium hydroxide and methyl iodide.



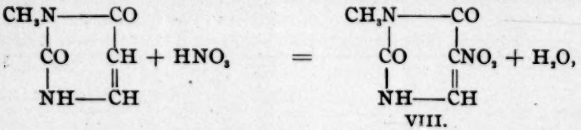
V.

When the mercaptopyrimidine, V., was digested with concentrated hydrochloric acid, it was converted quantitatively into 1-methyluracil, VII., with evolution of ethyl mercaptan.



VII.

The structure of the methyluracil, VII., and the corresponding mercapto derivative, V., was shown in the following manner: It was converted smoothly into 1-methyl-2,6-dioxy-5-nitropyrimidine,[2] VIII., by treatment with fuming nitric and sulphuric acids. Our nitromethyluracil, VIII.,



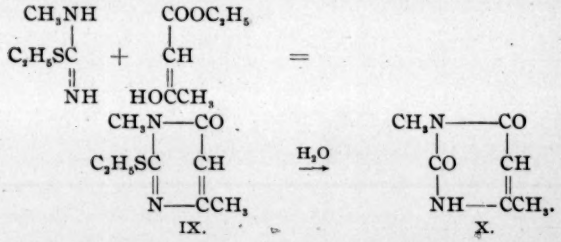
VIII.

was anhydrous and melted at 264°–265°. The isomeric

[1] Wheeler and Merriam: *Loc. cit.*
[2] Behrend and Thurm: *Loc. cit.*

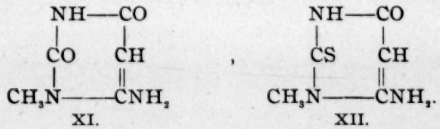
3-methyl-2,6-dioxy-5-nitropyrimidine[1] contains 1 molecule of water of crystallization and melts at 255°–256°.

Methyl pseudoethylthiourea condensed with ethyl acetoacetate to give 1,4-dimethyl-2-ethylmercapto-6-oxypyrimidine, IX. Its structure was confirmed by the fact that it was converted into Behrend's β-dimethyluracil or 1,4-dimethyl-2,6-dioxypyrimidine,[2] X., by treatment with hydrochloric acid.



IX. X.

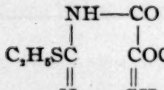
It is interesting to note that methylurea and methylthiourea condense with ethyl cyanacetate to give 2,6-dioxy-3-methyl-4-aminopyrimidine,[3] XI., and 2-thio-3-methyl-4-amino-6-oxypyrimidine,[4] XII., respectively,



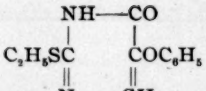
XI. XII.

It was shown in a previous paper[5] that pseudoethylthiourea condenses with diethyl formylglycollate to form 2-ethylmercapto-5-ethoxy-6-oxypyrimidine, XIII. We find that ethyl formylphenoxyacetate[6] also condenses with this pseudothiourea to give 2-ethylmercapto-5-phenoxy-6-oxypyrimidine, XIV.:

[1] Behrend and Thurm: *Loc. cit.*
[2] Behrend and Dietrich: *Loc. cit.* Behrend and Thurm: *Loc. cit.*
[3] Conrad: Ann. Chem. (Liebig), **340**, 314.
[4] Traube and Winter: Archiv. Pharm., **244**, 11 (1906).
[5] Johnson and McCollum: J. Biolog. Chem., **1**, 437.
[6] Johnson and McCollum: *Loc. cit.*



XIII.

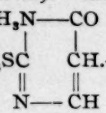


XIV.

EXPERIMENTAL PART.

Methylpseudoethylthiourea Hydriodide, $CH_3NHC(SC_2H_5):NH.HI$, was prepared by treating monomethylthiourea with ethyl iodide. It was obtained as a heavy oil, which finally solidified in a vacuum over sulphuric acid. The salt was extremely hydroscopic and on prolonged exposure to the atmosphere changed to an oil.

1-Methyl-2-ethylmercapto-6-oxypyrimidine,



—Molecular proportions of the above pseudourea hydriodide and the sodium salt of ethyl formylacetate were separately dissolved in the least possible quantities of cold water. The 2 solutions were then combined and treated with an aqueous solution containing 1 molecular proportion of potassium hydroxide. The mixture was allowed to stand at ordinary temperatures for about 12 hours and then heated for a few hours on the steam bath. No crystalline material deposited on cooling. The mercaptopyrimidine was extracted with ether and the ether allowed to evaporate spontaneously, when the pyrimidine deposited in prismatic crystals. They were extremely soluble in hot alcohol and in ether, but soluble with difficulty in cold water. The pyrimidine deposited from alcohol in stout prisms, that melted at 79°–80°, without effervescence, to a clear oil. It was soluble in dilute hydrochloric acid and was precipitated from the acid solution by phosphotungstic acid. Analysis (Kjeldahl):

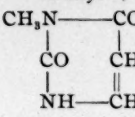
	Calculated for $C_7H_{10}ON_2S$.	Found.
N	16.47	16.6

The same mercaptomethylpyrimidine was also obtained when 2-ethylmercapto-6-oxypyrimidine[1] was treated with methyl iodide under the following conditions: One molecular proportion of potassium hydroxide and 9.8 grams of 2-ethylmercapto-6-oxypyrimidine were dissolved in 50 cc. of 95 per cent alcohol. Twelve grams of methyl iodide were then added and the solution digested on the steam bath until it gave no alkaline reaction with turmeric. It was then cooled, the insoluble potassium iodide separated by filtration and the excess of alcohol removed by evaporation on the steam bath. We obtained a syrup that would not solidify on cooling. After treatment with a small volume of water, to remove any potassium iodide, the mercaptopyrimidine deposited in well-developed prisms. They were crystallized from alcohol and melted at 79°–80°, to a clear oil. When mixed with the above mercaptopyrimidine the melting point was not changed. Analysis (Kjeldahl):

	Calculated for $C_7H_{10}ON_2S$.	Found.	
		I.	II.
N	16.47	16.33	16.6

2-Ethylmercapto-6-oxypyrimidine was recovered unaltered after heating with 1 molecular proportion of methyl iodide for 2 hours, at 155°–165°.

1-Methyl-2,6-dioxypyrimidine (*1-Methyluracil*),



—One and five-tenths grams of 1-methyl-2-ethylmercapto-6-oxypyrimidine were digested with 15 cc. of 20 per cent hydrochloric acid until the evolution of ethyl mercaptan ceased. When the acid solution was evaporated to dryness the methyluracil deposited in microscopic, prismatic crystals that melted sharply at 174°–175°, without effervescence, to a clear oil. It was extremely soluble in cold water and alcohol but insoluble in benzene. It was not

[1] Wheeler and Merriam.

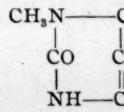
precipitated from its aqueous solution with picric acid. It was dried for analysis at 110° (Kjeldahl):

	Calculated for $C_5H_6O_2N_2$.	Found.
N	22.22	22.21

When uracil was heated with 2 molecular proportions of methyl iodide at 186°–200°, for 2 hours, it was recovered unaltered.

	Calculated for $C_4H_4O_2N_2$.	Found.
N	25. 0	24.74

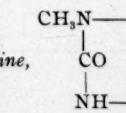
1-Methyl-5-nitro-6-oxypyrimidine,[1]



— Four and three-tenths grams of 1-methyluracil were dissolved in a mixture of 15 cc. of fuming nitric acid and 15 cc. of concentrated sulphuric acid, and the solution heated on the steam bath until effervescence practically ceased. The acid solution was then poured upon crushed ice, when a heavy, granular precipitate deposited. The compound was soluble with difficulty in cold water, but deposited from hot water in stout, prismatic crystals that melted at 264°–265°, with effervescence, to a clear oil. It deposited from hot alcohol in hexagonal plates. When the compound was mixed with some nitrouracil the melting point was lowered to 240°. It did not contain water of crystallization. Analysis (Kjeldahl):

	Calculated for $C_5H_5O_4N_3$.	Found.
N	24.56	24.8

1-Methyl-2,6-dioxy-5-brompyrimidine,

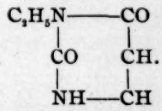


— One gram of methyluracil was dissolved in 8 cc. of glacial acetic acid and 1.3 grams of bromine added. Hydrobromic acid was evolved at once and the bromine derivative deposited

[1] **Behrend and Thurm**: *Loc. cit.*

in prismatic crystals. The compound was soluble in hot water but insoluble in cold. It deposited from 95 per cent alcohol in well-developed, transparent prisms that melted to a clear oil, at 228°–229°. Analysis (Kjeldahl):

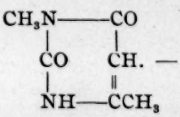
	Calculated for $C_6H_9O_2N_2Br$.	Found.
N	13.65	13.68



1-Ethyl-2,6-dioxypyrimidine (1-Ethyluracil),

—This compound was prepared from 2-ethylmercapto-6-oxypyrimidine as follows: The mercaptopyrimidine was first converted into 1-ethyl-2-ethylmercapto-6-oxypyrimidine by treatment with potassium hydroxide and ethyl iodide, as in the preparation of 1-methyl-2-ethylmercapto-6-oxypyrimidine. The diethylmercaptopyrimidine was obtained as an oil, which, without purification, was digested with concentrated hydrochloric acid until the evolution of ethyl mercaptan ceased. When the hydrochloric acid was removed by evaporation the ethyluracil was obtained as a crystalline deposit. The yield was practically quantitative. It was very soluble in hot water and alcohol. It deposited from benzene in foliated prisms that melted at 173°–174° to a clear oil. Analysis (Kjeldahl):

	Calculated for $C_6H_8O_2N_2$.	Found.
N	20.00	19.75



1,4-Dimethyl-2,6-dioxypyrimidine, — This compound has been prepared by Behrend and his co-workers.[1] We obtained it by condensing methylpseudoethylthiourea with ethyl acetoacetate to form 1,4-dimethyl-2-ethylmercaptopyrimidine. When this mercaptopyrimidine was boiled with concentrated hydrochloric acid the dimethyluracil was formed

[1] *Loc. cit.*

with evolution of ethyl mercaptan. It deposited from hot water in prismatic crystals, that melted at 260° to an oil. The compound agreed in its properties with Behrend's 1,4-dimethyluracil. Analysis (Kjeldahl):

	Calculated for $C_6H_8O_2N_2$.	Found.
N	20.00	20.00

Sodium Salt of Ethyl α-Phenoxy-β-oxyacrylate, $NaOCH:C(OC_6H_5)COOC_2H_5$.—Three and two-tenths grams of sodium wire and 1 molecular proportion of absolute alcohol, 6.3 grams, were digested in anhydrous ether until the formation of sodium ethylate was complete. Twenty-five grams of ethyl phenoxyacetate and 10.3 grams of ethyl formate were then added and the ether solution allowed to stand over night, when a colorless, crystalline sodium salt deposited. It was dried in a desiccator over sulphuric acid. Analysis:

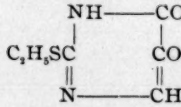
	Calculated for $C_{11}H_{11}O_4Na$.	Found.
Na	10.00	9.65

The free ethyl ester was obtained as a heavy oil when an aqueous solution of the sodium salt was treated with sulphuric acid. It underwent decomposition when we attempted to distil it under diminished pressure.

Hydrazone of Ethyl Formylphenoxyacetate, $C_6H_5NHN:CHCH(OC_6H_5)COOC_2H_5$.—Five grams of ethyl formylphenoxyacetate and 3 grams of phenylhydrazine were warmed together in a water-bath, for 30 minutes. They reacted with evolution of heat to form a yellow, crystalline compound. It deposited from warm, 95 per cent alcohol in yellow prisms, that melted at 219°–221°, with violent effervescence. Analysis (Kjeldahl):

	Calculated for $C_{17}H_{18}O_2N_2$.	Found.
N	9.39	9.3

2-Ethylmercapto-5-phenoxy-6-oxypyrimidine,



densing pseudoethylthiourea, in aqueous solution, with the sodium salt of ethyl α-phenoxy-β-oxyacrylate. After standing for 6 hours and acidifying with acetic acid, the pyrimidine deposited in prismatic crystals. It crystallized from alcohol in transparent prisms, that melted at 159° to an oil. It responded to a test for sulphur. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{12}O_2N_2S$.	Found.
N	11.29	11.06

NEW HAVEN, CONN.,
Feb. 15, 1907.

THE PREPARATION OF POTASSIUM FERRICYANIDE.

BY WILLIAM JAY KARSLAKE.

Two laboratory methods for the preparation of potassium ferricyanide from potassium ferrocyanide seem to be in more or less general use. The one treats the aqueous solution of potassium ferrocyanide with the required amount of either chlorine or bromine, while the other uses a solution of bleaching powder or potassium permanganate, in the presence of hydrochloric acid. At their very best either method gives only fair results and students often fail to get any pure potassium ferricyanide. This difficulty, however, may be overcome by using a dilute aqueous solution of potassium permanganate without the addition of any acid whatever. Somewhat more, about 10 per cent, potassium permanganate is taken than that calculated from the following equation:

$$6K_4Fe(CN)_6.3H_2O + 2KMnO_4 + H_2O = 6K_3Fe(CN)_6 + 2MnO_2 + 8KOH.$$

The method is as follows: To 50 grams of crystallized potas-

sium ferrocyanide, dissolved in 750 cc. of water, is added 7 grams of potassium permanganate, previously dissolved in 250 cc. of water. The mixture is heated on the water bath for about an hour, the precipitated manganese dioxide filtered off, the filtrate evaporated upon the water-bath to crystallization, *i. e.*, to about 150 cc., filtered again if necessary, and allowed to cool. Beautiful, large, red crystals of potassium ferricyanide separate. Yield 25–30 grams, or about 75 per cent of the theory.

UNIVERSITY OF IOWA,
Feb., 1907.

REPORT.

A Development of the Atomic Theory which Correlates Chemical and Crystalline Structure and Leads to a Demonstration of the Nature of Valency.

Crystallographers have long felt that some fundamental laws must underly the orderly phenomena of crystallography, while chemists have been not less impressed with the belief that the laws governing crystal forms must ultimately throw important light upon the problems of molecular structure. Hitherto, no far-reaching generalizations have been successfully proposed concerning the relations of crystal forms to molecular structure, although many efforts have been made in that direction. Messrs. William Barlow and William Jackson Pope, in a paper bearing the above title, have recently offered such generalizations based upon extended investigations.[1] Their conclusions, if confirmed by further researches, must have far-reaching effects upon chemical and crystallographic conceptions.

Because of the importance of the paper, the review of the article will be preceded by a brief statement of certain earlier views of crystal structure upon which these authors base their work.

Earlier Views of Crystal Structure.

In 1850 Bravais,[2] preceded by Delefosse, proposed a theory of crystal structure which has since been termed the "Raumgitter" theory ("space lattice-work" theory). It is based upon the well-known law that all properties of a crystal are

[1] J. Chem. Soc., **89**, 1675 (1906).
[2] Memoire sur les systems formes par des points distribués régulièrement sur un plan on dans l'espace, Paris: 1850.

alike in parallel directions. If these properties are dependent upon the nature and arrangement of the crystal molecules, it follows that like crystal molecules have like arrangement in all parallel directions. The structure of crystals thus suggested is illustrated in the accompanying diagram (Fig. I.), where the points represent the centers of gravity of the

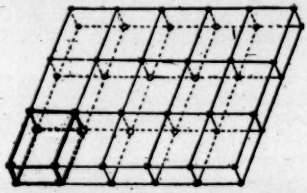


Fig. I.

various molecules, or rather the centers of rest about which the centers of gravity of the molecules may be considered to move. These molecules are discussed as if at rest.

Fourteen types of arrangement were shown to be possible according to this theory, falling into the 7 well-known crystal systems. As, however, recent work has shown that 32 groups of symmetry exist, it is manifest that the view of Bravais is inadequate to explain all the types of symmetry.

In 1879 Sohncke[1] proposed a further elaboration of the preceding theory. He suggested that several similar "Raumgitters" may be thrust, one into the other, thus producing more complex structures. All possible arrangements were developed by him by the following method. The "Raumgitters" are viewed as first brought into coincidence, and then one displaced from the other by one of three kinds of motion: (1) Translation, in a straight line; (2) rotation of each point of one "Raumgitter" about the corresponding point in the other; (3) a screw motion producing a combination of rotation and translation. In the second case an axis of rotation would exist between each pair of points, while, in the third case, screw axis would develop in similar positions.

Sohncke showed, further, that it is possible in this manner to develop 65 types of arrangement and that they fall into the 32 groups and 7 systems of crystals, in which observation shows that all actually existing crystals are classified. The theory of Sohncke has been further developed by Barlow.[2]

[1] Entwecklung einer Theorie der Krystalltructur. Leipzig: 1879. *Vide*, Also Sohncke: Z. f. Kryst., **20**, 445 (1892).

[2] Z. f. Kryst. u. Min., **23**, 1.

Volume and Dimensions of Molecular Space Units.

It can readily be seen, by inspecting Fig. I., that each "Raumgitter" may be viewed as made of units, built up as bricks in a house, to form the completed crystal structure. One of these units is indicated in Fig. I. by heavier lines. Each molecule will be seen to appropriate a space equal to one of these space units, the volume of which is often spoken of as the *molecular volume*. It has been shown that it is possible to calculate the relative volumes of these space units by the following equation:

$$\text{Molecular volume} = \frac{\text{molecular weight.}}{\text{density}}$$

The relative dimensions of the space unit, moreover, may be derived from the measurements of the 3 crystallographic axes, together with a consideration of the physical properties of the crystal, cleavage, etc. Thus, in the general case of a triclinic crystal, illustrated by Fig. II., the 3 edges of the space

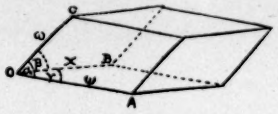


Fig. II.

unit will usually be parallel and proportional to the directions of the 3 crystallographic axes, a, b, c.[1] In this case the following equations hold:

$$OA : OB : OC = a : b : c,$$

and $COB = \alpha$, $COA = \beta$, $AOB = \gamma$, where α, β, γ, are the angles between the 3 crystallographic axes $c:a$, $c:b$, $a:b$, respectively. Let $OA = x$, $OB = \psi$, $OC = \omega$, then, by a well-known geometrical theorem,

$$V = x\,\psi\,\omega \sin\alpha \sin\beta \sin\gamma \quad \text{whence}$$

$$x = \sqrt[3]{\frac{a^2 V}{c \sin\alpha \sin\beta \sin\gamma}}$$

$$\psi = \sqrt[3]{\frac{V}{a\,c \sin\alpha \sin\beta \sin\gamma}}$$

$$\omega = \sqrt[3]{\frac{c^2 V}{a \sin\alpha \sin\beta \sin\gamma}}$$

[1] *Vide* Groth: Einleitung in die chemisch Kryst., 26.

In this manner the 3 relative dimensions, x, ψ, ω, of the space unit are known. By the use of the above formulae it is possible to investigate the changes in configuration which the molecular space units undergo, when various substitutions occur. The following illustration will make the method clear. Ammonium iodide crystallizes in the isomeric system in cubes, with a cubic cleavage, whence the space unit is cubic. Its molecular weight = 143.83, density = 2.501, whence, molecular volume $= \frac{143.83}{2.501} = 57.51$. Now the 4 hydrogen atoms can be replaced by methyl groups, yielding tetramethylammonium iodide, $N(CH_3)_4I$, which crystallizes in the tetragonal system with a tetragonal cleavage. These salts yield the following data:[1]

	Mol. vol.	x :	ψ :	ω
NH_4I	57.51	3.860	3.860	3.860
$N(CH_3)_4I$	108.70	5.319	5.319	3.842

It will be seen that the value of ω is the same in both cases, while the value of x and ψ have increased in the second compound, showing that the 4 methyl groups have entered the molecule in the plane of the axes a and b (horizontal plane) while the vertical (c) direction, is practically unaffected. In a similar manner, it is possible to investigate the configuration of the space units in various bodies and determine what changes various replacing atoms or groups produce.

The work of Barlow and Pope is based upon the foregoing conceptions concerning crystal structures and molecular configuration. We now proceed to a review of their investigation.

Fundamental Conceptions.

Two fundamental conceptions are presented in the paper:

1. In any chemical body the relative volumes of the atoms are proportional to their valencies. In other words, *valency expresses relative atomic volumes*. Thus, in the molecules of benzene the volume of each carbon atom is 4 times that of each hydrogen atom.

2. In any crystallized body the atoms are "close-packed;" *i. e.*, they are so placed as to occupy the least possible volume.

These conceptions are discussed in 3 aspects: (1) Atomic volume, (2) crystal structure, and (3) the deduced chemical principles.

[1] Slavek: Z. f. Kryst., 36, 368 (1902). Groth: Einleitung in die Chemische Kryst., p. 32, 1904.

I. Atomic Volumes.

The authors first show that the atomic volume of the same element may vary in different bodies. Thus Tutton, in his work upon alkali sulphates, obtained the following data:

	Mol. vol.	*a* :	*b* :	*c*
K_2SO_4	64.91	0.5727	1	0.7418
Cs_2SO_4	84.58	0.5712	1	0.7531

In substituting caesium for potassium the molecular volume is seen to increase, while the molecular configuration, as shown by the axial ratio, remains unchanged. But since the caesium enters the molecule in a definite position, it seems impossible that the configuration of the molecule should remain constant unless the sulphuric group expands *in the same ratio in which the molecular volume increases*. Hence, the conclusion is drawn that the absolute atomic volume may vary in different chemical bodies though, the ratio of the volume of any constituent to the volume of the molecule may remain constant, as in the case cited. The authors proceed to investigate the relative volumes of the atoms in the same molecule, the absolute volumes not being discussed.

Method of Investigation.

In order to investigate the relation, if any, which may exist between relative volume and valency, the authors reduce all molecular volumes to volumes proportional to the sum of the valencies of the constituent atoms, which they term the "valency volumes." If there is a constant relation between valency and relative volume it should be discovered in this way. The method of procedure is as follows:

Let V = volume of molecule and W = valency volume sought. Dividing the equation

$$V = x\psi\omega \sin\alpha \sin\beta \sin\gamma$$

by V, reduces to unit volume; multiplying the latter by W converts it into the volume W, proportional to the valency. Whence $W = x', \psi', \omega' \sin\alpha, \sin\beta \sin\gamma$. Let $x' = x$, $\psi' = y$ and $\omega' = z$, then

$$W = xyz \sin\alpha \sin\beta \sin\gamma.$$

The quantities x, y, z are termed "equivalence parameters." They are the 3 dimensions of the molecular volume when reduced to a volume proportional to the valency W. From the above value of W we obtain the following:

$$x = \sqrt[3]{\frac{a^2\,W}{c \sin\alpha \sin\beta \sin\gamma}}$$

$$y = \sqrt[3]{\frac{W}{ac \sin\alpha \sin\beta \sin\gamma}}$$

$$z = \sqrt[3]{\frac{c^2\,W}{a \sin\alpha \sin\beta \sin\gamma}}.$$

Fig. III. will make the above relations clear.

Volume V, sides x, ψ, ω. Volume W, sides x, y, z.

Fig. III.

Since the lengths of the axes determined by crystallographic measurements express ratios, not different numbers, it is permissible to multiply or divide them. The authors do this rather freely in securing their results, the factors not being entirely free from arbitrary elements.

Using the above method, the authors show that in any molecule *the relative volumes of the atoms are proportional to their valencies*. The evidence adduced is as follows: All cases of substitution may be reduced to 2 types, (1) those in which the sum of the valencies of the substituting and substituted atoms or groups is the same, *e. g.*, in the substitution of hydrogen by chlorine and (2) those in which the sum of their valencies differ, *e. g.*, in the substitution of hydrogen by methyl.

In substitutions of the first types the results show that no change occurs in the configuration of the molecule. This is illustrated by the following data:

	V	W	a	: b	: c	x	: ψ	: ω	: x	: y	z
Cl_3CCCl_3	113.34	14	0.5677	1	0.3160	4.8713	8.5808	2.7115	2.4260	4.2733	1.3503
Cl_3CCBr_2Cl	116.72	14	0.5612	1	0.3171	4.8760	8.6884	2.7551	2.4047	4.2849	1.3587
Cl_2CBr	120.16	14	0.5646	1	0.3192	4.9647	8.7949	2.7520	2.4090	4.2669	1.3620
Br_3CCBr_3	131.83	14	0.5639	1	0.3142	5.1099	9.0618	2.8472	2.4197	4.2911	1.3483
Br_3CCHBr_2	126.46	14	0.5650	1	0.3118	$\beta = 91°19'$			2.4294	4.2995	1.3406

In the above bodies the values of x, y, z remain essentially constant, showing that, though the absolute volumes of the molecules vary, the configuration of the molecules undergo no change. This indicates that the ratio of the volumes of the substituting and substituted atoms, to the volume of the molecule is constant, otherwise the configuration of the molecule would change. Hence, hydrogen, bromine and chlorine, possessing the same valency, occupy the same relative volume in the molecule, *i. e., their relative volumes are proportional to their valencies.* A number of other bodies were examined and found to conform to the same law.

In cases of the second type, in which the sum of the volumes of the substituting and substituted atoms differ, the relative dimensions of the molecule are found to change, the change in volume being proportional to the change in valency in the bodies studied. Thus in the minerals Chondrodite, Humite and Clinohumite, the following data are obtained:

	W.	a :	b :	c	x :	y :	z	z/W
Chondrodite, $Mg_9(SiO_4)_2{}^2Mg(FOH)$	38	1.08630	1	3.14472	2.4249	2.2323	7.0199	0.18473
Humite, $Mg_8(SiO_4)_2{}^2Mg(FOH)$	54	1.08021	1	4.40334	2.4278	2.2475	9.8965	0.18327
Clinohumite, $Mg_7(SiO_4)_2{}^2Mg(FOH)$	70	1.08028	1	5.65883	2.4349	2.2540	12.7547	0.18221

These minerals differ by a constant increment, Mg_2SiO_4, having the composition of the Fosterite, which is seen to enter the molecule in the z direction, the x and y values remaining nearly constant. The volume of the molecule is, therefore, proportional to the value of z. But the ratio of z: W is constant, hence the ratio of the volume to the valency is constant, *i. e., the volume is proportional to the valency.* Assuming this principle the authors find it possible to predict the axial ratios a: b: c and the value of x: y: z, in the other number of the series, Prolectite and Fosterite, and find that the calculated values approximate to those observed very closely, as shown by the following data:

	W		a :	b :	c	x :	y :	z
Prolectite, $Mg(SiO_4)_2{}^2Mg(FOH)$	22	observed	1.0803	1	1.8862	2.3877	2.2102	4.1689
		calculated	1.0822	1	1.8500	2.4292	2.2446	4.1526
Fosterite, Mg_2SiO_4	16	observed	0.9296	1	1.1714	2.4492	2.2769	2.8691
		calculated	0.9240	1	1.1804	2.4292	2.2446	2.8674

Two very interesting results are derived from the law thus discussed:

(1) In a number of cases it is shown that water of crystallization causes the expansion of the molecule in one direction, indicating that, in such bodies, the water of crystallization enters the crystal structure in layers.

(2) In the formation of double salts there is usually a simple numerical relation between the valency values of the components, which is shown by the authors to result geometrically from close packing. Thus, in potassium alum,

$$K_2SO_4.Al_2(SO_4)_3.24H_2O,$$

we have the valencies of the parts in the ratio 14:36:96 = 1:3:8.

The general conclusion reached is that, *in any molecule the atoms have volumes proportional to their valencies.*

II. Crystal Structures.

The second principle is that atoms combine in crystals in such a manner as to produce close-packed assemblages. This arrangement springs from the nature of the atoms and the forces uniting them. They are viewed as elastic bodies, acted upon by 2 opposing forces, the attractive forces exerted between them, and the repulsive forces which are designated by the term "elasticity" of the atoms. Under the action of these 2 forces it is held that the atoms would arrange themselves in such a manner as to produce an assemblage occupying the minimum space, *i. e.*, they would be "close-packed."

The principle employed in determining what structure will be assumed by any given number of atoms is, therefore, to ascertain what arrangement will produce close-packing.

In case two or more arrangements are possible, which are nearly equally close-packed, each may occur, thus explaining the phenomenon of polymorphism.

In order to give a mechanical picture, the atoms are represented as elastic spheres which are compressed by the force named, in entering into combinations. In reality, it is assumed that no space exists between them.

In their paper the authors discuss a considerable number of compounds of the aromatic series, promising to publish later results upon extended studies of members of other series which they have already investigated, and which, they state,

confirm the conclusions here presented. Their methods may be sufficiently indicated by considering a few of the bodies which they discuss. Of these the most important is benzene, C_6H_6.

Chemical Structure.

The carbon atoms possess a valence of 4 and will have, according to the preceding discussion, 4 times the volume of the hydrogen atoms. Close-packing of such an assemblage will result when the 6 carbon atoms are so placed that each occupies the center of the face of a cube, while the hydrogen atoms occupy the solid angles of the cube. As, however, there are 6 hydrogen atoms and 8 solid angles, it follows that 2 of the angles must be unoccupied. These form the opposite ends of the same diagonal. In the drawings the molecule is so placed that this diagonal is vertical. Fig. IV. shows a model of the benzene molecule, while Fig. V. is a diagram illustrating the arrangement of the atoms in it.

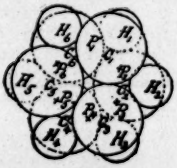


Fig. V.

In assembling these molecules to form the crystal structure, 2 slight distortions are produced which assist in close-packing. In the first distortion the hydrogen atoms are pressed inwards, separating the carbon atoms as illustrated in Fig. VI*a*. In the second distortion the molecules are slightly compressed in one horizontal direction as shown in Fig. VIII.

The molecules are assembled as follows: They are first placed in vertical piles as shown in Fig. VII., the first distortion assisting in this process. These piles are then placed side by side so that alternate tiers, *b*–*b* in Fig. VIII., stand one-

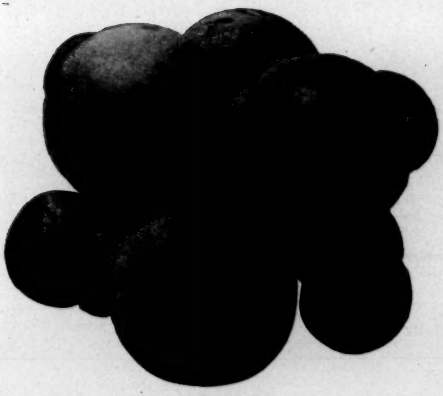


Fig. IV.

fourth molecule higher than those of the other tiers, *a–a*. In this manner the projecting angles of one pile correspond to

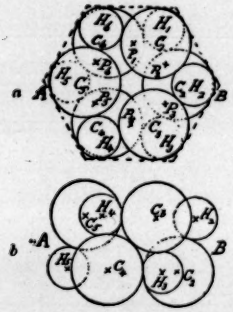


Fig. VI.

the reentrant angles between the adjacent molecules. The second distortion assists in this process. The resulting arrangement

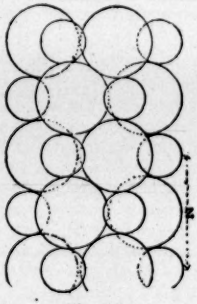


Fig. VII.

is that believed to exist in the benzene crystals. It is illustrated in Fig. VIII., representing one horizontal layer of mole-

cules. In such a structure it is possible to predict not only the system and group in which the substance will crystallize, but its axial ratios as well.

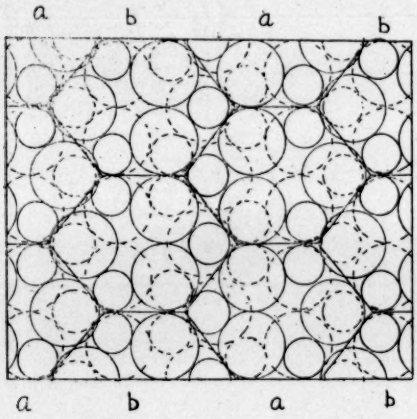


Fig. VIII.

Crystal System.

In Fig. IX. let the intersections of the diagonals represent the centers of gravity of the molecules of Fig. VIII. The diagram then shows the "Raumgitter" as seen in a horizontal plane. The structure represented is seen to possess 3 rectangular directions of symmetry. These consist of the following: (1) Three sets of twofold screw-axes of symmetry, of which 2 lie in the plane of the drawing, indicated by the signs ●—● and ●– – –●, and one perpendicular to it, passing through the centers of the molecules, shown by the signs ●. (2) Three systems of planes of symmetry, 2 perpendicular to the plane of the drawing, shown by the solid lines, and 1 parallel to it. The presence of the latter may be detected by inspecting Fig. VII. Two of these systems of planes are planes of gliding symmetry. All crystals possessing this type of symmetry must belong to the normal group of the orthorhombic system.

Observation shows that benzene actually crystallizes in that system and group.

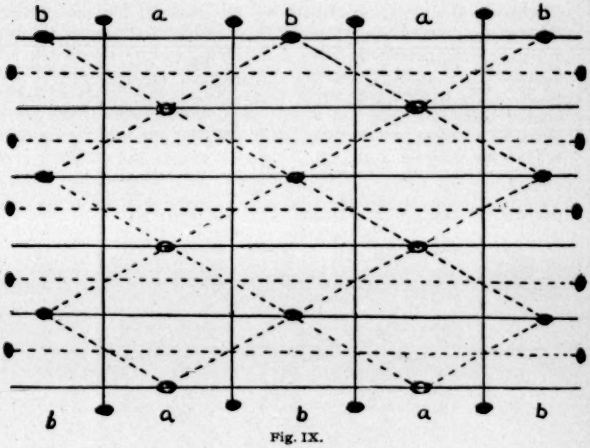


Fig. IX.

Axial Ratio.

The x and y dimensions of the "Raumgitter" unit may be seen by inspecting Fig. X., while the value of z may be ob-

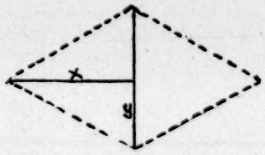


Fig. X.

served in Fig. VII. The drawing shows that these possess the values $x = 3.101$, $y = 3.480$, $z = 2.780$, respectively. Inserting these values in the formulae on p. 643, we find $a : b : c = 0.891 : 1 : 0.799$. The same values are experimentally obtained by measuring the crystals of benzene. The view pre-

sented thus receives confirmation from the fact that the crystal symmetry and axial ratios developed theoretically, are identical with those actually observed in the benzene crystals.

Among other bodies studied by the authors are the halogen derivatives of benzene, the dihydroxyl derivatives pyrocatechol, 1,2-$C_6H_4(OH)_2$, resorcinol, 1,3-$C_6H_4(OH)_2$, and hydroquinol, 1,4-$C_6H_4(OH)_2$, triphenylamine, $(C_6H_5)_3N$, triphenylmethane, $(C_6H_5)_3CH$, triphenylbromide $(C_6H_5)_3CBr$, and triphenylacetic acid, $(C_6H_5)_3CCOOH$. Among these, triphenylmethane is of peculiar interest, as showing the manner in which complex molecules may be built up. Fig. XI. shows the authors' con-

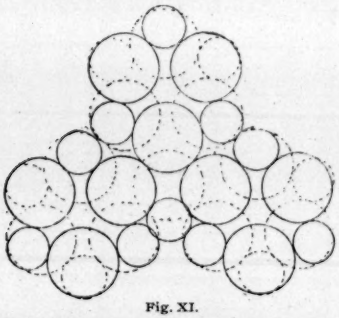


Fig. XI.

ception of the molecules of this substance. All of these bodies are found to give results similar to those already studied.

The authors also offer a simple explanation of the formation of the multiple benzene rings, naphthalene, Fig. XII., and anthracene, Fig. XIII., and promise a later discussion of their derivatives.

III. Chemical Equivalency.

The authors show that such close-packed assemblages possess 3 geometrical properties which find expression in certain fundamental chemical facts. The latter are: (1) Equivalency; (2) multivalency; (3) partitioning of the molecules.

(1) *Equivalency.*

In a close-packed assemblage of spheres, single spheres or groups of spheres may be so situated that they can be re-

moved homogeneously, without affecting the arrangement of others. Into the cavities thus formed other spheres of like

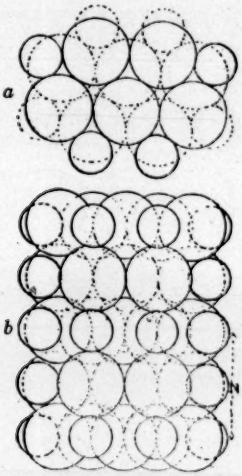


Fig. XII.

volume may be inserted, thus reproducing the original arrangement. This is illustrated by Fig. XIV. Chemically, this

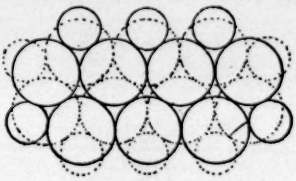


Fig. XIII.

will give rise to equivalency, since atoms can replace others of the same volume in a molecule, without change of structure. Valency itself may be viewed as the expression of the relative volume of atoms. The stability of arrangement of

such related substitution products leads to the likeness of crystal form termed *isomorphism*. Hence, both equivalency

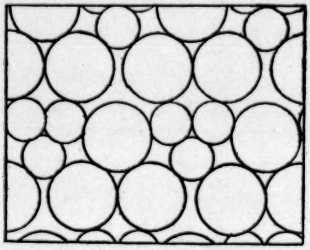


Fig. XIV.

and isomorphism are given a natural explanation by the first geometrical principle.

Certain facts indicate, however, that equivalent atoms, though nearly equal, may differ slightly in volume. Thus Tutton found the following results in his work on the alkali sulphates and selenates:

	V	W	x :	y :	z
K_2SO_4	64.91	12	2.2109	2.1977	2.8463
Rb_2SO_4	73.34	12	2.2049	2.1899	2.8648
Cs_2SO_4	84.58	12	2.2003	2.1826	2.8777
K_2SeO_4	71.67	12	2.2207	2.2083	2.8204
Rb_2SeO_4	79.94	12	2.2147	2.1957	2.8412
Cs_2SeO_4	91.09	12	2.2112	2.1900	2.8524

The differences in the values of x, y, z indicate slight differences in the configurations of the molecule and hence, slight differences in the volumes of the atoms of potassium, caesium and rubidium. The differences are seen to be progressive and indicate that the atomic volumes may change slightly in the same group in the periodic classification, data being given to show that the volume probably increases with increasing atomic weight.

These principles interpret many hitherto unexplained facts, numerous examples being given to illustrate the discussion of the following:

(1) The difference in crystal form of the acids and many of their salts, *e. g.*, sulphuric acid and potassium sulphate. This

fact is explained by the difference in the volumes of the hydrogen and potassium atoms.

(2) The isomorphism of salts of different acids, as in the plagioclase feldspars, $NaAl_2Si_3O_8$ and $CaAl_2Si_2O_8$. Here it is seen that NaSi and CaAl have the same volume and, hence, can replace each other in the molecule.

(3) The isomorphism of elements in complex bodies, though not observed in simple bodies.

(4) The variation observed in crystal form, when replacing atoms have the same valency volume but differ much in form, *e. g.*, in the substitution of nitro, NO_2, by methyl, CH_3.

(2) *Multivalency.*

The second geometrical property may be stated as follows: When like spheres are removed homogeneously from an assemblage and replaced by larger spheres or groups of spheres, the walls of the cavity will be made to gap. Close-packing can only be restored by inserting new spheres in the gap so produced. The authors show that the volume of the latter will be equal to the difference in volume of the replaced and replacing spheres. If V = volume of sphere replaced, then the volume of replacing spheres, to produce close-packing, will equal V, $V + 1 + 1 = V + 2$, $V + 2 + 2 = V + 4$, or $V + n + n = V + 2n$; *i. e.*, the *volume of the replacing atoms differ by intervals of* 2.

Chemically, this principle is expressed by the law of multivalency, that the valencies of an element differ constantly by intervals of 2. Thus, if, in a cavity occupied by an atom of valency m, another atom of the valency 1 be inserted, a second atom of valency 1 is required to fill the gap produced, or if atoms of valency 2, etc., be inserted, additional atoms of the same valency are required to restore close-packing. In other words, the original atom will function as having a valency of m, $m + 2$, $m + 4$, etc., though throughout the operation its volume has not changed. Thus the change of valency by intervals of 2 is fully explained and involves no variation in the actual volume of the atom. In this manner caesium can combine with iodine in CsI, CsI_3, CsI_5, CsI_7, CsI_9, while having a constant volume of 1.

The second geometrical principle is further illustrated in the valencies of radicals. Thus in the replacement of a hydrogen atom by an oxygen atom in ethane, the further addition of an atom of valency 1, such as hydrogen, is required, producing alcohol, C_2H_5OH. Again, in 3 molecules of benzene, H_3 may be substituted by N to produce triphenylamine,

$(C_6H_5)_3N$, but if a carbon atom take the place of H_3 an additional hydrogen atom must be added as is seen in triphenylmethane, $(C_6H_5)_3CH$. The isomorphism of such salts as sodium nitrate, $NaNO_3$, and calcium carbonate, $CaCO_3$, is similarly explained.

(3) *Partitioning of Molecules.*

In the partitioning a close-packed structure of atoms, it may be possible to separate them into molecules in several ways. Various interesting reactions are explained by this principle. This may be illustrated by the formation of the meta-, ortho-, and paradiderivatives of benzene. Let Fig. XV. represent a vertical pile of benzene molecules, the carbon

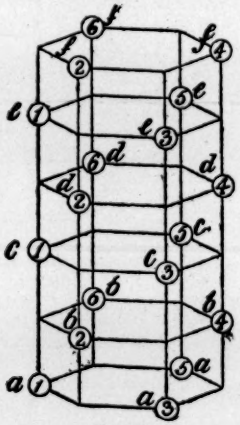


Fig. XV.

atoms being numbered 1, 2, 3, etc. These atoms can be partitioned into benzene molecules by separation between the planes *ab*, *cd*, etc., or between the planes *bc*, *de*, etc. If replacements occur in the positions 3 and 5, both methods of partitioning will give meta products. If, however, replacements occur in the position a_1, b_4, c_2, d_6, e_5, f_2, etc., the 2 methods of partitioning give, respectively, ortho- and paradiderivatives. Thus may be explained the fact that meta diderivatives are formed alone, while ortho- and paradiderivatives are so frequently produced in the same reaction. The authors

promise a later discussion of problems of dissociation based upon this principle.

In conclusion, the authors consider the crystal form of the elements and the relation of the crystalline and amorphous states.

The communication thus summarized is characterized by the wide range of the data discussed, the fruitfulness of its conceptions and the fundamental character of its principles. If correct, these principles must be of universal application and, hence, susceptible of verification at many points. Until they have had such further investigation it would seem proper to withhold judgment, especially in view of the necessary brevity with which the authors have presented their results, and the fact that they have promised further publication in the near future. The character of the work done, the remarkable confirmation offered quantitatively, and the number of facts which it correlates, afford strong presumptive evidence of the correctness of the fundamental conclusions advanced. If the work is so confirmed, the paper will prove to be one of the most important contributions to chemical and crystallographic conceptions which has appeared in recent years.

CHARLES K. SWARTZ.

REVIEWS.

POST'S CHEMISCH-TECHNISCHE ANALYSE. Handbuch der analytischen Untersuchungen zur Beaufsichtigung chemische Betriebe, für Handel und Unterricht. Dritter vermehrter und verbesserter Auflage. Herausgegeben von PROF. DR. BERNHARD NEUMANN. Grossherzoglich technische Hochschule, Darmstadt. Mit zahlreichen eingedruckten Abbildungen. Erster Band. Erster Heft und zweiter Band, Erster Heft. Braunschweig: Friedrich Vieweg und Sohn. 1906. pp. 180 and 208. Price, M. 4.80 and M. 5.50, respectively.

The earliest edition of this work was among the first to bring together, in handy form, the analytical methods employed in the various branches of manufacturing chemistry. In this, and in the second edition, Dr. Post was assisted in the preparation of the material by specialists in different industries. The present edition, although prepared at Dr. Post's suggestion, is brought together by Dr. Neumann without his immediate cooperation, but with the assistance of a considerably larger number of specialists. The plan and general scope of the book remains the same as in the earlier issues, but the entire work has been rewritten and considerably amplified. The editor and his co-laborers have sought to include selected methods and to present the subject matter in concise form. So far as is practicable, the materials in-

volved in each industry are considered under 3 headings: Raw Materials, The Manufacturing Process, and The Finished Product. The work is to be published, as before, in 2 volumes of convenient size, each to include 4 sections, of which the first for each volume is at hand. These sections, each containing the analytical methods relating to certain allied industries, are obtainable in separate form, a rather unusual concession on the part of the publishers.

The subject matter of the first section (Heft) of Volume I. includes the following chapters: Water and Sewage (38 pp.), by Prof. Dr. J. H. Vogel, of Berlin; Fuels (34 pp.), by Dr. H. Langbein, of Niederlössnetz-Dresden; Pyrometrie (36 pp.), and Chimney, Producer and Blast Furnace Gases (72 pp.), both by Dr. B. Neumann, the editor.

The first section of Volume II. treats of the following topics: Lime, Limestones, Cements and Gypsum (80 pp.); Earthenware (92 pp.), and Glass and Glazes (36 pp.), all by Drs. H. Seger and E. Cramer, of Berlin.

The methods given are, naturally, those in use in German laboratories and these differ in some instances from American practice, but this does not seriously lessen the value of the revised volumes. The treatment of the various topics appears to be essentially uniform, although one notices an unfortunate tendency on the part of some of the specialists to omit references to original papers. The text of the previous edition has been but little reproduced in this one, and the whole has been so completely worked over that there has been opportunity to bring the procedures up to date. The revised handbook is well worthy the attention of all practicing chemists, as well as of teachers and students. The remaining sections are promised at an early date and will be awaited with interest.

H. P. TALBOT.

VORTRÄGE ÜBER DIE ENTWICKLUNGSGESCHICHTE DER CHEMIE VON LAVOISIER BIS ZUR GEGENWART. Von A. LADENBURG. Braunschweig: Friedrich Vieweg und Sohn. Pp. 117. 1907. Price, M. 12.

Ladenburg's history is so well known to chemists that it is only necessary to call attention to the fact that it has now appeared in a new edition. The preface is of special interest and may be reproduced advantageously.

The author says: "In issuing the fourth edition of this book, about thirty-eight years after the publication of the first edition, it must be confessed that this is done with a certain feeling of sadness.

"When the first edition appeared in the year 1869 the great chemists Liebig, Wöhler, Bunsen, Kolbe, Kekulé, Dumas,

Wurtz, Frankland, Williamson, all of whom I knew personally, and some of whom I could call my teachers, were still living. To-day not only are these dead, but many of my distinguished contemporaries, with some of whom I have worked, as Friedel, Grimaux, Beilstein, V. Meyer, and others, have passed away, and a younger generation, for the most part unknown to me personally, now holds the helm. Hence the feeling of sadness with which I submit this book to the consideration of my colleagues.

"It appears to me meanwhile as though the quiet, certain course of our science has become rapid and tumultuous, and as though the haste and effort that characterizes modern life have also made themselves felt in science. The historian is especially conscious of this condition and it increases his difficulties very greatly in the attempt to gain an objective view and to find the essential that really advances the science. Yet I have believed and considered it to be in accordance with the character of the book that I should follow the development of chemistry down to the present day, and therefore I have added the seventeenth lecture."

This seventeenth lecture has to do with new conceptions of valence, with the calculation of chemical equilibria by means of thermal measurements, solid solutions, allotropy, albumen, catalysis, the chemistry of colloids, etc. I. R.

VAN NOSTRAND'S CHEMICAL ANNUAL, 1907. A Handbook of useful data for Analytical, Manufacturing and Investigating Chemists, and Chemical Students. First Year of Issue. Edited by JOHN C. OLSEN, A.M., Ph.D. With the cooperation of eminent chemists. New York: Van Nostrand Company. 1907. Pp. x + 496. Price, $2.50 net.

The date in the title of this book is apt to prove misleading; the preface was printed November, 1906, a considerable proportion of the contents of the book, so far as they can be identified, refer to 1905 and it is issued in the latter part of March, 1907. The "eminent chemists" referred to are the following: Messrs. A. F. Seeker, E. E. Reid, C. A. F. Kahlbaum, A. Rogers, V. J. Chambers, J. L. R. Morgan, G. P. Pegram and C. H. Lips. The contents of the book consist of the usual tables arranged in the manner customary in works of this class, and containing, as the editor naively remarks, such data as "cannot generally be carried in the mind, but must be readily accessible for use." Considerable experience with them would be necessary in order to form an opinion of their accuracy. The table of the formulae and properties of organic compounds does not make a good impression. Aside from certain peculiarities of selection, which

are, perhaps, inevitable, the nomenclature is, in many instances, open to grave objection; to the reviewer the list conveys the impression that it has been made from the German source by one whose familiarity with the subject is limited, and is *not* the familiarity of an organic chemist. Be this as it may, the translation of many of the names of compounds is done very poorly and incorrectly; moreover, they are stated to have been taken from the third edition of Beilstein's "Handbuch," which is, of course, obsolete so far as much of the data required for this "Annual" is concerned. No mention is made of the use of the supplementary volumes of "Beilstein" and, so far as the reviewer has been able to check the data, these volumes do not appear to have been employed. It is hardly possible to believe that this can be the case, but if so, it is entirely inexcusable.

Leaving this point, the question may fairly be asked, "Why use 'Beilstein' at all?" The value of a book such as the one under review lies almost entirely in its data possessing the highest possible degree of accuracy; without this it is worse than useless, and such accuracy can only be obtained by the most careful, laborious collation of the original sources of the facts in question.

A "Review of Chemical Literature" and a list of "New Books," American and English, and of "Foreign Books, mostly German," form the concluding section of the "Annual" and constitute a novelty in compilations of this nature.

The "review" consists of the titles of papers without any other indication of the nature and scope of their contents; obviously, the specialist does not want this kind of thing and it is difficult to understand who else would do so, whereas its omission would have reduced the weight and also, presumably, the price of the volume. The hypothetical purchasers of the "Annual" are, or ought to be members of the American Chemical Society and they, therefore, receive real *reviews* of all important chemical books, annual reports of the progress of chemistry in all its principal branches, with copious references to the literature, and "CHEMICAL ABSTRACTS."

It is a pleasure to praise, without reserve, two features of the volume. The frontispiece consists of an admirable reproduction of a photograph of Sir William Ramsay. The type of the book is clear and the form, paper and binding are attractive. In these respects it is a decided advance on some other chemical works issued by this firm of publishers.

J. BISHOP TINGLE.

A HISTORY OF CHEMISTRY. By F. P. ARMITAGE, M.A., F. C. S., late Exhibitioner of Magdalen College, Oxford. Assistant Master at St. Paul's School. London and New York: Longmans, Green & Co. 1906. Pp. 266. Price, $1.60 net.

Mr. Armitage has written a volume which will be of decided value to students. There was need for a clearly written, brief history of chemistry in English, suited to those who have neither the time nor the knowledge of chemistry requisite for a study of the works of Meyer or Kopp.

This book is well proportioned; it gives little space to the earlier history of chemistry, but from the time of Priestley and Lavoisier is sufficiently full. It concludes with the development of organic and stereo-chemistry, not including modern physical chemistry. Brief sketches of the lives of leading chemists add to the interest of the volume. The author's style is lively and clear. Quotations from the Berzelius-Wöhler letters and from similar sources bring the men, the time and the work near to the reader. Mr. Armitage's history can be warmly recommended to students. E. R.

PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS, VOL. I. By HARVEY W. WILEY, A.M., Ph.D., Chief Chemist, U. S. Dept. of Agric., Washington, D. C. Easton, Penn.: The Chemical Publishing Co. 1906. Pp. 636. Price, $4.00.

The first volume of this work is devoted exclusively to soils. Part I. deals with the more common minerals, the classification and characteristics of rocks and, finally, with the process involved in the transformation of the latter into soil, the organic constituents of soils being given a brief review. This part would find a more natural place in a work not devoted primarily to a consideration of methods of soil examination, but rather in a distinctive text-book on the origin and properties of soils. Nevertheless, it will serve a valuable purpose for such students as have not previously been taught the elements of mineralogy and geology in their relation to this subject.

Part II. deals very fully and satisfactorily with the entire question of sampling, the importance and value of which in soil investigation cannot be too much emphasized.

In the third part the discussion is not confined to methods, but much of the material presented is of a general character. In this part the author deals with physical properties and with the relations of soils to heat and moisture.

The subject of mechanical soil analysis is treated very fully in the fourth part, descriptions being given in detail not only of the more modern, but also of the earlier methods,

in order that the student may familiarize himself with the history of the development of this line of investigation.

Part V. is devoted to the subject of the relations of gases and soils, and deals with questions of absorption, diffusion and methods for the determination of carbon dioxide.

Part VI. begins with a discussion of various miscellaneous determinations such as water, organic matter in its several forms, free organic acids, acidity, etc.; this is followed by a full treatment of the different solvents which have from time to time been recommended for use in soil analysis, and by the various methods for determining the individual mineral constituents which are thereby extracted from soils. Considerable space is likewise devoted to the methods for the determination of nitrogen, amine nitrogen, ammonia, and the volatile nitrogenous compounds of soils. This part closes with a compilation of the soil methods of the Association of Official Agricultural Chemists of the United States.

The subject of nitrification is treated most exhaustively in the seventh part. The discussion deals with the formation of ammonia, the sources of nitrates, the steps involved and the physical and chemical conditions favorable to their formation, the methods and apparatus employed in the study of the nitrifying organisms, methods for determining the nitrifying power of soils and, in fact, with practically every phase of the subject. At the close, the methods for determining nitrous and nitric acid are treated in a full and comprehensive manner.

In the last part the author describes the methods for examining soil waters. Space is also devoted to the special treatment of peat soils and the methods of analysis adapted thereto, and this is followed by a description of the determination of some of the other elements found in certain soils, such for example, as copper, lead, zinc, strontium, boron and titanium.

On the title page of this volume the author speaks of the work as "A Manual for the Study of Soils, Fertilizers, and Agricultural Products, for the Use of Analysts, Teachers and Students of Agricultural Chemistry," from which it will be seen that he did not intend to confine himself to a presentation of mere methods of analysis.

Aside from the first part, the work is far better adapted for advanced students than for beginners, and even the former will use it to best advantage under the direction of an experienced analyst or teacher.

The author has given a critical review of certain methods, but in many instances this has been obviously impossible, much as it might be desired from the standpoint of the inexperienced analyst. This omission is, in some cases, nevertheless, regrettable.

The book seems to be fairly free from typographical and other errors, though a serious mistake is observed at the top of p. 378. The work is a distinctly valuable addition to the agricultural chemical literature and takes rank with the best works of its class in Germany. It will be welcomed with gratitude by all agricultural students and investigators, as well as by specialists in other lines and, owing to the many changes and additions, will be a valuable acquisition even to those who possess the first edition. H. J. WHEELER.

RADIOACTIVE TRANSFORMATIONS. By E. RUTHERFORD, D.Sc. LL.D., F.R.S. MacDonald Professor of Physics, McGill University, Montreal. With Diagrams. New York: Charles Scribner's Sons. 1906. Pp. 287. Price, $3.50 net.

The contents of this book formed the subject matter of a course of 11 lectures delivered by Rutherford, at Yale, in March, 1905, on the Silliman Foundation. The author has selected the more interesting facts and theories in connection with radioactivity and has presented them in a clear and interesting style.

After an introductory lecture, the order of treatment is as follows: Radioactive Changes in Thorium; The Radium Emanation; Transformation of the Active Deposit of Radium; Active Deposit of Radium of Slow Transformation; Origin and Life of Radium; Transformation Products of Uranium and Actinium and the Connection between the Radioelements; The Production of Helium from Radium and the Transformation of Matter; Radioactivity of the Earth and Atmosphere; Properties of the α-Rays; and the Physical View of Radioactive Processes.

While the subject matter is, in general, presented in such form as to be intelligible to those who are not mathematical physicists, yet the treatment is strictly scientific and frequently involves the use of the calculus. This work is, however, much less mathematical than the "Radioactivity" by the same author.

This book is, of course, authoritative, since it comes from one of the leading workers in the field.

It is heartily recommended to all who have a good knowledge of general physics, and an elementary knowledge of the higher mathematics.

Certain mechanical errors in the printing will, doubtless, be removed in subsequent editions. H. C. J.

QUALITATIVE ANALYSIS AS A LABORATORY BASIS FOR THE STUDY OF GENERAL INORGANIC CHEMISTRY. By WILLIAM CONGER MORGAN, Ph.D. (Yale), Assistant Professor of Chemistry in the University of California. New York: Macmillam Co. 1906. Pp. 351. Price, $1.90 net.

The purpose of this book is best explained by quotations from the preface. "This text presents the course of instruction given by the author to the Freshman classes at the University of California where the exigencies of vocational courses render it impracticable for a large number of students to devote more than one year to general inorganic chemistry and to qualitative analysis as well. Therefore the scheme of qualitative analysis is made to serve as a means of correlating the apparently independent experiments of general chemistry. * * * The course presupposes good chemical training in the secondary schools * * "

"The method of presentation is based principally, though not exclusively, upon the theory of electrolytic dissociation."

The methods used for the separations are the familiar ones. The book seems well suited to its purpose. E. R.

DIE HARZE UND DIE HARZBEHÄLTER MIT EINSCHLUSS DER MILCHSÄFTE. By A. TSCHIRCH. Second Edition. Leipzig: Gebrüder Borntträger. 1906. Two volumes. With 104 illustrations. Pp. xxii + 1268. Price, M. 32.

The appearance, in 1900, of Tschirch's "Die Harze und die Harzbehälter," a well developed volume of some 400 pages, marked a distinct epoch in the literature of this extensive but very vague and unsystematized subject. The second edition of the book shows a remarkable growth to 2 volumes of more than 1200 pages. It is a model of the printer's art, both in type and in illustration. The proof has been carefully read and only an occasional error is noted, such as the substitution of "Shipping" for "Chipping," on page 562. Numerous references to the literature of the subject make the book a most valuable bibliography, and the comfort of the reader is materially increased by the substitution of text figures for the plates at the end of the earlier edition. The omission of the method for Tschugaff's cholesterin reaction, page 1091, is in striking contrast with the completeness of detail which characterizes the book. A feature of the new edition is the compilation, well illustrated, of methods employed in the production and collection of the principal resins. Additional studies of 50 secreta, including the milky juices, such as gutta percha and caoutchouc, help to swell

the number of pages. In a praiseworthy spirit of enabling others to repeat, and possibly to correct his work in this difficult field, the author has included details of methods of investigations together with analytical results, the book thereby assuming the character of a laboratory guide.

The fortunate combination of chemist and botanist gives to Prof. Tschirch special qualifications as a leader in such lines of investigation. In the hope of gaining a better foundation for future studies of a more thorough character, his policy in the past has been to broaden rather than to deepen our knowledge of these substances. The difficulties of such work are great, due, primarily, to the fact that so many of the substances are amorphous and without sharp melting points. A distinct service has been rendered, however, by insistence that only specimens of known origin should be studied and that deductions should be based on the behavior of the individual constituents of resins rather than on that of the mixtures from which they are obtained.

The fact that work has only begun in this field is evidenced by the following: The author leaves open the question of the hydroxyl or carboxyl character of resin acids, nor can he decide between $C_{19}H_{28}O_2$ and $C_{20}H_{30}O_2$ as the correct molecular formula for abietic acid. In view of this uncertainty, he holds that any structural formula for the latter is purely conjectural, although many facts point to its being a derivative of an octohydroretene. The relation of ethereal oils to the resins which they accompany is not yet clear, nor can a resin be considered as formed from tannins on the simple evidence that the latter occur near the secretion cells. The author rightly holds that knowledge of the exact chemical character of each class is still too limited to justify such reasoning. In view of such uncertainties it is not a matter of wonder that but little progress has been made in the synthesis of resins.

In the botanical section of the book the views on the seat of resin production and on resin flow are of particular interest. The foundation of this botanical work is the improbability that resins and ethereal oils diffuse through membranes impregnated with water. Several years ago the author demonstrated that the seat of resin production is not in the interior of certain cells from which it is excreted through the membranes of adjacent cells into the intercellular spaces, but lies rather in a well defined, mucilaginous layer, "resinogen Schicht," lining the secretion cells. Numerous subsequent studies have confirmed this view and shown that resins do not wander from cell to cell. The views upon resin flow are of fundamental importance from both scientific and indus-

trial points of view. The author divides resins into two classes. First, "physiological resins," occurring in the normal secretion cells, "primary resin ducts," which form in the plant throughout its growth but yield only a very limited quantity of resin; second, "pathological resins," flowing from "secondary resin ducts," formed in large numbers in the new wood after the infliction of a wound. These secondary ducts are of schizogenous origin and increase in diameter lysigenously. They form an anastomotic system from 5 to 6 cm. in length, opening upon the wound both from above and below. By far the greatest part of the resin flow is from such pathological ducts.

From the fact that secretion cells are formed even in terminal buds, where all available material is needed for forming new wood, and from the further fact that once formed the secreta undergo no further change during the course of vegetation, these secreta are not to be considered as waste products of normal metabolic assimilation, but serve some useful biological end.

All in all, a truly great book is presented to us, a book which will prove itself indispensable to every worker in this field.

CHAS. H. HERTY.

A METHOD OF TEACHING CHEMISTRY IN SCHOOLS. By A. M. HUGHES, B.Sc., Science Mistress of the L. C. C. Secondary School, Eltham, and R. STERN, B.Sc., Science Mistress of the North London Collegiate School. Cambridge: The University Press. 1906. Price, $1.00.

This little book will be found of value not only to teachers of chemistry but also to teachers of nature study in the grades. Educational journals reiterate the words "from the known to the unknown," but few show clearly the practical steps to be taken. The authors of this book, however, have worked out a clear, well-organized plan, starting with common, everyday objects and leading from these into more technical science.

The method of the book is suggestive and for this reason will be helpful even to teachers who do not follow its plan in detail. The authors' idea is to let the teacher take the part of guide, or supervisor, in his classes, allowing the children to create their own problems. Any one using this method will find that he must have a very definite plan for his work, but a plan so elastic that he will find it difficult, if not impossible, to follow closely any book.

Much of the work in the first part of the volume, such as that with limestone, slate, sandstone, etc., might be made more vital to children if used in connection with their geography. The same is true of the simpler experiments on solution

and crystallization, which can first be used to advantage in explaining the formations around hot springs and geysers.

The attempt to make the children thoroughly familiar with the chemical characteristics of substances is good, as it secures a sure foundation for more advanced chemistry. One of the chief reasons that chemistry is a difficult subject for many students is due to the fact that the materials used are unfamiliar. It is almost impossible to reason in a science of which the alphabet, so to speak, is unknown. What meaning, for instance, is conveyed to the average mind by the words "sodium hydroxide." The student, however, who has once made the substance out of entirely familiar materials and known its characteristics from childhood, is in a position to use the compound intelligently. The advanced student has no time for these preliminary steps, steps necessary, however, to a thorough knowledge of the science.

The book, with its suggestiveness, can be highly recommended to all teachers of science to children.

M. DRAEGE.